A145 645   NATIONAL FUEL CELL SEMINAR (1983) PROGRAM AND ABSTRACTS   1/
            HELD AT ORLANDO FLORIDA ON 13-16 NOVEMBER 1983(U)
            DEPARTMENT OF DEFENSE WASHINGTON DC   1983

UNCLASSIFIED   F/G 10/2   NL
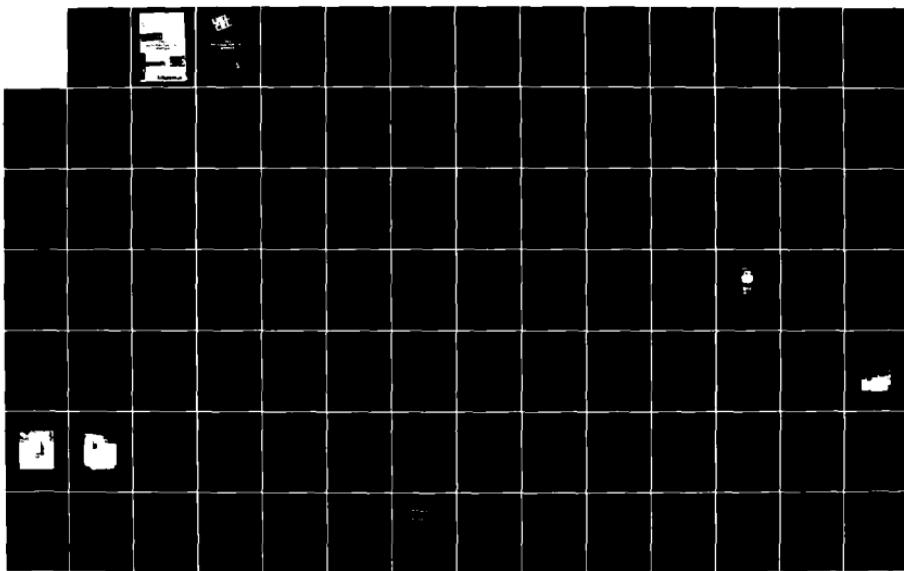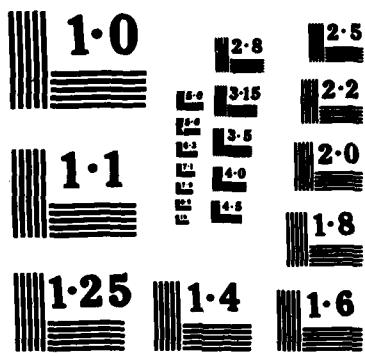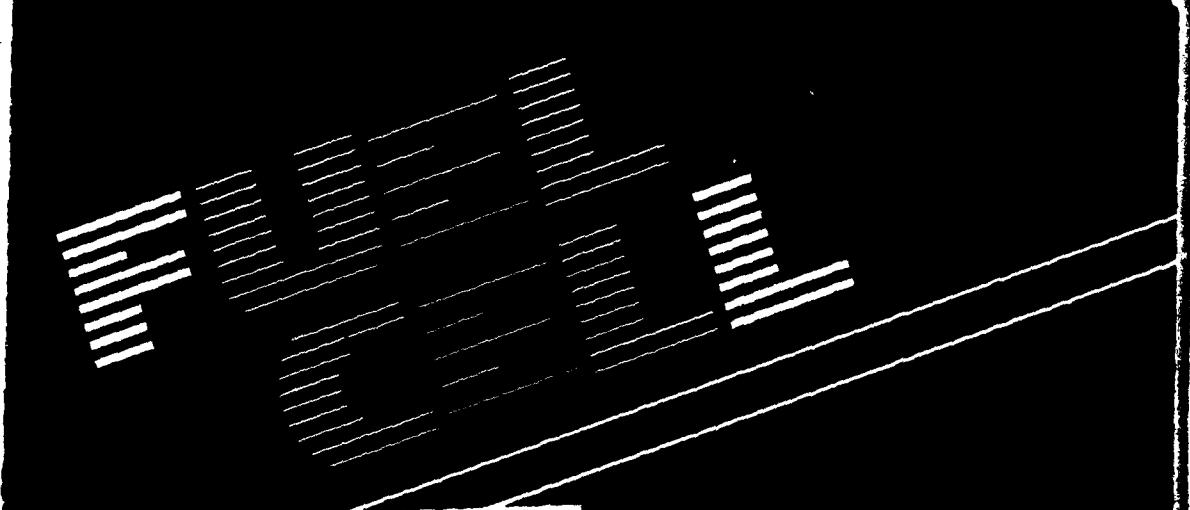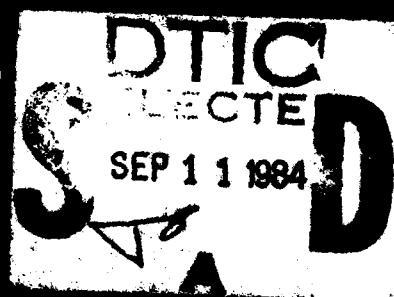
FUEL CELL

1983
NATIONAL FUEL CELL
SEMINAR

ABSTRACTS

FUEL CELL

1983
NATIONAL FUEL CELL
SEMINAR

PROGRAM AND ABSTRACTS

November 13-16, 1983
Americana Dutch Resort Hotel
Orlando, Florida

In Cooperation with

Department of Defense
Department of Energy
Electric Power Research Institute
Gas Research Institute
National Aeronautics and Space Administration

DTIC
ELECTE
SEP 1 1 1984

A

SEMINAR COORDINATED by COURTESY ASSOCIATES, INC., WASHINGTON, D.C.

8:00 a.m.   CONTINENTAL BREAKFAST

8:30 to 10:00 a.m.   SESSION 1-A: OPENING SESSION

                       Chairman: John J. Cuttica,
                                  Gas Research Institute

                       • Welcome and Introductory Remarks
                       • Keynote Address by Robert S. Kripowicz, Staff Director,
                         Energy Development and Applications Subcommittee of
                         the Science and Technology Committee, U. S. House of
                         Representatives
                       • Fuel Cell Activities in the USA

10:00 a.m.   COFFEE BREAK

10:30 to 12:00 Noon   SESSION 1-B: TECHNOLOGY STATUS

                       Chairman: Graham Hagey,
                                  U.S. Department of Energy

                       This session will provide the background
                       information on the status of fuel cell
                       technology for the seminar.

                       • Acid Fuel Cell Technology – An Overview 1
                         A. J. Appleby, Electric Power Research Institute

                       • Molten Carbonate Fuel Cells – Development Status. . . 6
                         R. Dean Pierce and John P. Ackerman, Argonne
                         National Laboratory

                       • Solid Oxide Fuel Cells. 11
                         Darrell C. Fee and John P. Ackerman, Argonne
                         National Laboratory

12:00 to 1:30 p.m.   LUNCHEON

1:30 to 5:00 p.m.   SESSION 2: ON-SITE INTEGRATED ENERGY PROGRAM

                       Chairman: Vincent B. Fiore,
                                  Gas Research Institute

                       This session will provide a review of ongoing efforts
                       to develop, field test, and commercialize small fuel
                       cell power systems for use as commercial cogeneration
                       systems.

1:30 to 5:00 p.m. SESSION 2, continued

There will be a coffee break at approximately 3:15 p.m.

Note: *The following session will take place simultaneously with Session 2.*

1:30 to 5:00 p.m. SESSION 3: MOLTEN CARBONATE TECHNOLOGY

Chairman: John Ackerman,
           Argonne National Laboratory

This session will present the major results of the molten carbonate technology development efforts conducted over the past year.

1:30 to 5:00 p.m.   SESSION 3, continued

There will be a coffee break at approximately 3:15 p.m.

6:00 to 7:30 p.m.   CASH BAR RECEPTION FOR ALL PARTICIPANTS

7:30 a.m.   CONTINENTAL BREAKFAST

8:00 to 11:30 a.m.   SESSION 4: MULTIMEGAWATT POWER PLANTS

           Chairman: Jeffrey Serfass
                    The Fuel Cell Users Group of the
                    Electric Utility Industry, Inc.

This session will provide up-to-date information regarding the programs for development and demonstration of electric utility-size power plants.

    There will be a coffee break at approximately 10:00 a.m.

       Note: *The following session, 5-A&B, will take place simultaneously with Session 4.*

8:00 to 11:30 a.m.   SESSION 5-A: SOLID OXIDE TECHNOLOGY

           Chairman: John E. Sholes,
                    Morgantown Energy Technology Center

This session will provide the status of the solid oxide technology development with recent advances in tubular and monolithic systems being highlighted.

8:00 to 11:30 a.m.   SESSION 5-A, continued

SESSION 5-B: FUEL CELL MODELLING

Chairman: John E. Sholes,
                Morgantown Energy Technology Center

This session will provide an overview of computer-based
analytical tools currently being used to define fuel
cell technical and economic characteristics.

There will be a coffee break at approximately 10:00 a.m.

11:30 a.m.   Shuttlebus departs for luncheon at Walt Disney World.

12:00 to 1:30 p.m.   LUNCHEON

1:30 p.m.   Shuttlebus departs Contemporary Hotel for return to Seminar.

2:00 to 3:30 p.m.   SESSION 6-A: INDUSTRIAL USERS GROUP

Chairman: Gordon Liu,
                   The Dow Chemical Company

This session will provide the present status of the
newly formed industrial Fuel Cell Users Group, focusing
on industry interest in fuel cells.

"Fuel Cell Requirements for Various Industrial Applications"

"Fuel Cell for Industrial Applications - Manufacturers'
Perspective"

"Potential Industrial Fuel Cell Users Group Briefing"

There will be a coffee break at approximately 3:30 p.m.

4:00 to 5:30 p.m.   SESSION 6-B: SPECIAL APPLICATIONS

                        Chairman: Johann A. Joebstl,
                                     U. S. Army Mobility Equipment Research
                                     and Development Command

This session will provide a status of ongoing fuel cell programs aimed at space applications (NASA), defense applications (Army/Air Force), and a hybrid electric forklift.

2:00 to 5:30 p.m.   SESSION 7: ACID ELECTROLYTE FUEL CELL RESEARCH

                        Chairman: Marvin Warshay,
                                     NASA Lewis Research Center

This session will provide the status of the various acid electrolytes including phosphoric acid, advanced acids and solid polymers.

2:00 to 5:30 p.m.   SESSION 7, continued

There will be a coffee break at approximately 3:30 p.m.

5:30 to 6:30 p.m.   WINE AND CHEESE TASTING FOR ALL PARTICIPANTS

7:30 a.m.   CONTINENTAL BREAKFAST

8:00 a.m. to 12 Noon   SESSION 8:   STATUS OF JAPANESE FUEL CELL TECHNOLOGY

Chairmen: Edward Gillis,
           Electric Power Research Institute

           and

           Noboru Itoh,
           New Energy Development Organization

This session will update the seminar attendees on
the status of the Japanese Government-sponsored fuel
cell research and development program.

8:00 a.m. to 12 Noon   <u>SESSION 8, continued</u>

There will be a coffee break at approximately 10:00 a.m.

12:00 Noon   ADJOURNMENT

ACID FUEL CELL TECHNOLOGY - AN OVERVIEW

A. J. Appleby
Electric Power Research Institute
Palo Alto, California

Introduction

In the 1982 National Fuel Cell Seminar, an attempt was made by
the present author to give an overview of the state-of-the-art
of acid fuel cell materials technology up to that time. This
presentation represents an update of the pre-1982 work. How-
ever, the limited means of the EPRI materials technology pro-
gram (and that of other funding organizations, for example,
NASA and GRI), together with the consequently low number of
man-hours available for this advanced work, has dictated that
new ideas have far outstripped practical progress in the area
of advanced acid fuel cell components. For example, EPRI-
funded projects in this area, expressed in constant 1983 dollars,
totaled about $650K per year in 1979-80 and about $600K per year
in 1982-83. In 1984, the anticipated sum will be only about
$400K. This clearly dictates limited practical possibilities
for improving the potential heat-rate of the acid fuel cell
beyond presently specified values (at both UTC and Westinghouse,
about 8300 HHV Btu/kWh at close to end-of-life), at least with-
in a reasonable time.

Improvements in the heat-rate of the fuel cell are certainly the
key to wider anticipated commercial use. For example, if the
annual fixed costs of a fuel cell are $200/kW-yr, and the cost
of fuel (natural gas) is $7.00/$10^6$ Btu, then, based on the above
heat-rate and assuming 5000 h/y availability, a cell voltage im-
provement of 40 mV (5.5%, based on 1982 UTC estimates) gives the
same change in overall electricity cost as a 7.5% decrease in
total system capital cost. As repeat component technology im-
proves and capital cost reduces still further (the annual fixed
cost decreasing correspondingly), progressively smaller reduc-
tions in heat-rate will become increasingly important in deter-
mining the overall change in electricity cost. Progress in im-
proving system efficiency will therefore be ultimately more im-
portant in determining the overall competitiveness of the acid
fuel cell system as its overall capital cost is reduced.

Directions To Improving Heat-Rate in Phosphoric Acid Cells

As indicated in the 1982 abstract, higher fuel cell efficiency
in the future may require the use of higher cell temperatures
and pressures. While acetylene-black-based carbon supports for
the platinum or platinum alloy cathode catalyst are adequate at
205°C and 8 atmosphere pressure at a cell potential of 0.73V,
they are probably not suitable for use at the even higher cell
temperatures and consequent higher cell voltages required for
lower system heat-rates. In 1982, carbides and silicides were
examined as possible candidates for high-stability conducting
catalyst supports. The most satisfactory of these materials
to date has proven to be titanium carbide, studied under RP1200-
8 (Giner, Inc.). During the early part of 1983, this material
was successfully prepared in high-surface area form (equivalent

in terms of m^2/unit volume to better than the value for acetlyene
black, or about 100 m^2/g). The material has recently been suc-
cessfully catalyzed with high-surface area platinum catalyst,
thus far with very good results. Initial indications are that
the product is of very high stability, and has many of the prop-
erties of the platinum alloy or intermetallic materials pre-
viously studied under RP1200-5 (Lawrence Berkeley Laboratory).
It appears to show higher activity than platinum on a carbon
support on a per-unit-area basis, perhaps by as much as a factor
of five at constant potential under utility fuel cell conditions.
If this can be reproduced with practical high-surface-area cat-
alysts, an overall performance improvement of 60-70 mV at constant
current density may be anticipated. Future work will emphasize
further treatments in the hope of obtaining still higher activity.
This material appears to show a great deal of promise as an ad-
vanced catalyst which may eventually allow heat rate improvements
of (optimistically) up to 700 Btu/kWh, giving an ultimate end-
of-life value of 7600 Btu/kWh (HHV) for a negligible increase
in cell component cost. Such performance may require somewhat
higher cell operating temperatures in practice, to take advantage
of the improved corrosion behavior of the TiC support compared
with graphitized or chemically-treated carbon materials.

Such a higher performance catalyst layer may need changes in
other cell repeat components for operation at temperatures
over 205°C. However, unless electrolyte management can be very
carefully controlled (which is improbable) it will be difficult,
if not impossible, to make separator plates for these conditions
which have been prepared from graphite-resin mixtures carbonized
at low temperatures in the range 900-1200°C. Plates made in this
way are porous and have a relatively low corrosion resistance,
as studies under RP1200-2 (Stonehart Associates) have shown.
Other work conducted under RP1200-2 has demonstrated much lower
corrosion rates for certain fully graphitized materials, and more
particularly in recent work for dense glassy carbons prepared
at 2000°C. In particular, this work has shown the effect of boron
additives in giving enhanced "pregraphitization" and corrosion
resistance for samples of carbons heat-treated at lower temper-
atures.

A wide range of corrosion currents under utility fuel cell cathode
conditions is obtained on graphites of different origins and with
different preparation conditions. These corrosion currents also
vary with time, and are to a large extent associated with the
presence of porosity in the heat-treated material. However, as
shown during the past year by Engelhard Industries under NASA
contract DEN3-241, the sealing of surface porosity can reduce
initial corrosion rates of porous graphite materials by almost
two orders of magnitude to acceptable levels, although it is not
presently known if this improvement in corrosion rate will be
maintained as a function of time. However, the temperatures up
to 2900°C that are required to produce dense, corrosion-resistant

graphite represent a costly operation with a high reject rate,
thus some low-cost approaches to apply chemically resistant
non-porous coatings are being investigated under RP1200-1 at
present. These will use glassy carbon or chemical-vapor-
deposited (CVD) carbon coatings (RP1200-2) or conductive CVD
carbide coatings (RP1200-8) on bipolar plate components heat-
treated at lower temperatures in the 1200-1600°C range. Coat-
ings on other types of low-cost substrates are also being in-
vestigated.

If any of the above research is successful, it should allow
heat-rates on the order of 7600-7800 Btu/kWh to be attained in
"first generation" phosphoric acid electrolyte methane or light-
distillate fueled systems. If all of the research were sucess-
ful, it could lead to values perhaps as low as 7200 Btu/kWh in
cells operating at approximatley 240°C. Under these temperature
conditions, direct internal-reforming methanol cells with sim-
plified external chemical-engineering systems and with heat-
rates (HHV) on the order of 6800 Btu/kWh may eventually be
feasible.

Other Approaches To Improved Heat-Rates

Phosphoric acid does not possess all the properties of an ideal
fuel cell electrolyte. Since it is chemically stable and rel-
atively involatile at temperatures above 200°C and is CO_2 re-
hecting, it is useful in utility fuel cell power plants that
use fuel cell waste heat to raise steam for reforming natural
gas and liquid fuels. While it is the only common acid com-
biring the above properaties, it does show inferior performance
as an air electrode medium compared with other electrolytes,
including materials such as sulfuric and perchloric acids, whose
other chemical properties render them unsuitable for utility
fuel cell use.

Recent work points toward anion adsorption as the major contrib-
utor to the relatively poor catalytic performance of phosphoric
acid electrolyte, especially in the concentrated form present
in the utility fuel cell. For example, RP1676-2 (Lawrence
Berkeley Laboratory) has shown that the high oxygen electrode
activity of dilute trifluoromethane sulfonic acid is propor-
tionately reduced by addition of phosphoric acid at increasing
concentration. Under these conditions, the poisoning effect
on the reaction is so great that changes in the oxygen reduction
rate are seen at phosphate ion concentrations as low as 300 ppb.
However, while suggesting that adsorption influences the reac-
tion, this experiment showed neither the precise mechanism of
the interaction nor the effect of high concentrations of phos-
phate ion on the process.

Some of this uncertainty has been cleared up by work conducted
under RP1200-9 (Texas A&M University), which has recently ex-
amined phosphate adsorption in more concentrated solutions on

a platinum oxygen reduction catalyst by a radioactive technique.
Phosphate ion adsorbs on the platinum electrode surface at
potentials close to those at which high current densities for
oxygen reduction are noted, but is progressively desorbed at
higher potentials where the platinum surface becomes more ox-
idized. In contrast, the anion of trifluormethane sulfonic acid
appears to be hardly adsorbed on the unoxidized platinum surface,
but at higher potentials its adsorption is associated with oxid-
ation products of water (or reduction products of molecular
oxygen) on the electrode. This observation gives some clues as
to the type of interaction required for highly effective catal-
ysis. Work conducted under RP1200-7 (Case Western Reserve Univ-
ersity) during late 1982 has shown that addition of concentrated
trifluoromethane sulfonic acid to concentrated phosphoric acid
enhances the activity of the latter for oxygen reduction by
40 mV (which could improve the heat of first generation fuel cells
by 400 Btu/kWh). This contrasts with the earlier RP1676-2 results
reported above for dilute solutions, however, it shows the real
possibility that the catalytic activity of platinum-based catalysts
in phosphoric acid can be improved under utility fuel cell condi-
tions by the use of suitable additives, especially fluorinated
sulfonic or phosphonic acids. This work has very recently been
confirmed at Lawrence Berkeley Laboratory under RP1676-2 with a
mixture of one equivalent of tetrafluoroethane disulfonic acid
dihydrate with one equivalent of 85% phosphoric acid at 100°C.
Again, a 40 mW improvement over pure 85% phosphoric acid was
observed for oxygen reduction at constant current density. Effort
is continuing under RP1676-1 (ECO, Inc.) and RP1676-3 (SAI) to
synthesize suitable non-volatile, stable fluorinated sulfonic or
phosphonic acid compounds to replace phosphoric acid since tri-
fluoromethane sulfonic acid is much too volatile for practical
use. One year ago, there was some doubt as to the equivalence
of the activity of higher non-volatile members of the fluorinated
sulfonic acid family to that of the volatile lowest member of
the series, trifluoromethane sulfonic acid. Latest work under
RP1676-2 shows that their activities are equal, in the absence
of impurities resulting from byproducts of the synthesis. This
result allows some guarded optimism that the present research
will ultimately prove to be successful. Unfortunately, not all
research problems are resolved at this time. One serious dif-
ficulty that was not anticipated when this work started is that
under utility fuel cell conditions the conductivity of 95% phos-
phoric acid is more than 10 times higher than that of 89% tetra-
fluoroethane disulfonic acid (the dihydrate composition). Un-
fortunately, the conductivity values of the latter types of acid
appear to be the rule, with phosphoric acid the exception. One
consequence of this problem is that fuel cells operating on pure,
fluorinated sulfonic acids as electrolytes show better intrinsic
oxygen electrode activity than phosphoric acid, but at the same
time show higher cell resistance, thus negating their catalytic
advantage. Further understanding of the anomalously high con-
ductivity effect of phosphoric acid is therefore required, to

see if it can be extended to other materials. The effect appears
to be associated with the self-ionization of phosphoric acid, so
that the conducting species (protons) are associated with phos-
phoric acid molecules rather than with water molecules as in the
fluorinated sulfonic acids. Investigation of other additives
to "unlock" these protons and to increase their mobility to
levels similar to those in concentrated phosphoric acid is pro-
ceeding at the present time. This represents a very promising
avenue for future research with a high eventual pay-off.

MOLTEN CARBONATE FUEL CELLS - DEVELOPMENT STATUS

R. Dean Pierce and John P. Ackerman
Argonne National Laboratory
Chemical Technology Division
9700 S. Cass Ave.
Argonne, IL 60439

Molten carbonate fuel cell (MCFC) technology offers the potential for clean and efficient generation of electricity from hydrocarbon fuels and coal. Carbonates are attractive electrolytes because of their compatibility with carbonaceous fuels and their operating temperature range, which provides "waste heat" at a useful temperature (about 650°C). In 1975, the Department of Energy (DOE) joined the Electric Power Research Institute (EPRI) as a major sponsor of MCFC development. Research also has been sponsored by the Gas Research Institute (GRI), individual utilities, the State of New York, and internal corporate funds.

MCFC development has progressed to the point where (1) demonstrated single cell performance is highly attractive for power generation, and (2) the performance of cells in a well-functioning stack is about the same as single cells. A recent test of cell performance conducted by General Electric Company showed performance typical of state-of-the-art MCFC cells. Fuel composition was: 60% H_2, 40% CO_2 humidified at 60°C ± 3°C. Oxidant composition was: 75% air, 25% CO_2 humidified at 60°C ± 3°C. Fuel utilization and oxidant utilization were: 75% and 50%. Temperature was 650°C within 10 degrees, pressure was 1 atm; care was taken to assure that pressures were balanced. At a current density of 160 mA/cm^2, five of five cells achieved an average voltage that ranged from 750 to 776 mV. The theoretical maximum achievable voltage of an "essentially lossless" cell under these conditions would be 827 mV at any current density. United Technologies Corporation subscale stack tests, Nos. DOE-1 and DOE-2, have shown that performance of individual cells in a well-functioning stack agree with that predicted by models calibrated with the performance of individual isothermal cells.

The emphasis of the DOE program, therefore, was focused on the development of stacks of cells leading to the scaleup of components and manufacturing processes for MCFCs. Accordingly, two major contractors, United Technologies Corporation (UTC) and General Electric (GE), were selected and in 1979 were awarded DOE development contracts with the same four tasks: (1) develop a reference power plant design, (2) develop components and stack designs, (3) develop plans and fabrication facilities necessary for progressing to prototype-stack testing, and (4) verify cell operation on coal derived gas. The expectation is that the subsequent prototype testing of a full-size MCFC stack in about 1988 will be a joint venture between private industry and the government, and that this joint venture will be followed by a demonstration plant that will be largely financed with private funds.

The present program is concentrating heavily on
the development of subscale stacks. UTC has operated
several stacks and is developing solutions to the problems
uncovered.[1] GE is working on an alternative stack design
concept,[2] and Energy Research Corporation (ERC) is
developing MCFCs that will reform methane internally.[3]
This paper will review the status of these studies and
mention supporting work underway by these and other
researchers. More details of the individual research
programs will be presented in other papers in this seminar.

STACK DEVELOPMENT

The current UTC stack design incorporates external
manifolding of the gases. These manifolds seal against the
edges of the stack of cells with fiber-mat gaskets. UTC has
demonstrated excellent electrochemical performance of their
stacks, but electrolyte migration, end-cell shorting, and
anode "creep" have restricted stack life. The electrolyte
migration and cell shorting result from shunt currents within
the stack; therefore, design modifications have been proposed
to reduce such currents or their effects. UTC has found that
electrolyte is moved out of individual cells at the interface
between the anode and the electrolyte matrix. The driving
force for this process is the shorted electrochemical cell
operating between the anode gas and the gas in the adjacent
manifold. A portion of the electrolyte that is moved out of
the cells by this process is wicked back into the cell, some
accumulates at the edge of the cell, and some is wicked into
the manifold gasket. As a result of the voltage gradient up
the face of the stack, shunt currents occur in the manifold
gasket. Last year, UTC reported here that electrolyte was
lost from the bottom (positive) cells to the top of a stack,
DOE-2. The resultant drying of the bottom cells in the stack
destroyed stack performance. In addition, unequal flux of
lithium and potassium ions caused a fractionation of the salt
composition producing a relative enrichment in potassium ions
in the salt at the top of the stack. UTC has studied salt
migration during the past year with post-mortem examinations
and many out-of-cell tests. As they will report, manifold
seal and cell design modifications have greatly reduced the
shunt currents, and a compositional change in the carbonate
salt has eliminated the fractionation in salt composition.
Design changes proposed to reduce migration and harmful
deposition of corrosion products have also been made.

UTC assembled a new 20-cell stack that incorporates the
recent improvements, and this stack is scheduled to begin
operation in September. They are planning to operate a
100-cell subscale stack differing from this 20-cell stack
only in stack height. This stack work is supported by a
coordinated program between DOE and EPRI. GRI is planning
to support extended operation of one of these stacks to
examine additional endurance issues. These stacks will use
the conventional NiO cathode; however, a subsequent subscale
stack is planned to use an improved cathode material.

7

GE, under DOE support, has developed a calendering technique to produce thin (0.5 mm) electrolyte-matrix tapes and demonstrated excellent performance of 100-cm^2 cells assembled using these tapes. Their current emphasis is to assemble larger cells (about 1000 cm^2) using stackable hardware that incorporates their internal manifolding designs.

ERC, as reported here last year, has touted the advantages of internally reforming MCFCs. They currently have support from EPRI, GRI, and DOE to pursue such cells. They have demonstrated identical performance with methane and an equivalent simulated reformed feed in a 300-cm^2 cell. They are currently investigating alternative in-cell catalysts and catalyst-anode configurations and are evaluating the effects and control of carbonate wetting of the reforming catalyst. EPRI is supporting their work to develop internally reforming stacks.

SUPPORTING RESEARCH

Cathodes: Considerable attention is devoted to research on alternative cathodes because, as discussed in some detail at this seminar last year, the reference lithiated NiO cathodes will not survive the desired five years in pressurized cells because of slow dissolution and mass transport toward the anode. UTC, GE, ANL, Ceramatec, and Battelle Northwest are all studying alternative cathode materials, and ERC is studying the limitations for applying NiO.

Anodes: UTC, GE, and ERC are investigating means for increasing the creep strength and sinter resistance of anodes by incorporating oxides with nickel. The Institute of Gas Technology (IGT) and Nothwestern University, under EPRI support, are developing stabilized copper anodes.

Electrolyte: The use of thin (0.5 mm) electrolyte matrices of $LiAlO_2$ for the Li_2CO_3-K_2CO_3 has become standard, replacing the hot-pressed structures (tiles) that were used in the 1970's. UTC pioneered the development of tape-cast matrices under support by Niagara Mohawk. As mentioned earlier, GE produces thin tapes by a calendering process. ERC is evaluating both tape casting and electrophoretic deposition to produce their matrices. In addition to providing lower ionic resistance, the new matrices have been much more reliable and cross-leakage resistant than the hot-pressed tiles. This is principally due to the better particle distribution that is attained when the matrix is formed in the absence of the large amount of electrolyte present with hot pressing. Each of the contractors has worked out procedures for introducing electrolyte, burning out any binders, and providing adequate matrix support. GE has pioneered the investigation of $SrTiO_3$ as an alternative to $LiAlO_2$, and IGT has studied alternative carbonate salts.

8

Separator (bipolar) Plates: Another important materials problem is separator plate corrosion. Although UTC and GE have studied separator plate materials, budget restraints have curtailed that work temporarily. Currently, the reference material is a laminate of nickel (on the anode side) and a stainless steel (e.g., 310SS or 316SS). Corrosion of the stainless steels now used appears too great for long-term life. Also, uncertainties exist regarding the possible carburization of the steel because of the high carbon activity of the anode gas and the high carbon mobility in nickel. Carburization could cause delamination at the nickel-SS interface. GE has done some research on copper-SS laminates, which are cheaper and prevent carbon migration to the interface.

Seals: The present MCFC stack components have little springback capability to accommodate dimensional changes; this complicates component sealing and maintenance of good electrical contact. UTC and GE are giving considerable attention to providing reliable seals that can survive expected power and thermal transients.

Contaminants: UTC and IGT have studied effects of sulfur on fuel cell performance. IGT is continuing the evaluation of contaminant effects; they are planning both in-cell and out-of-cell tests to discriminate between and model the performance-decay mechanisms resulting from sulfur contamination.

SYSTEM STUDIES

There is a continuing need for systems evaluations to support the planning and evaluation of the fuel cell programs. Both GE and UTC have reported work under the first task of their DOE contracts. GE recently issued a topical report on their study,[4] which was done with Pacific Gas and Electric. The GE study describes a 650-MW coal-fired plant that is based on off-the-shelf components except for the fuel cell. It contains gas- and steam-turbine bottoming. The coal-to-bus bar efficiency was estimated to be 48% HHV, and the cost of electricity to be 60 mils/kWh. UTC presented a design employing a Lurgi gasifier (which generates methane-rich gas) and a "sensible heat reformer"--a UTC concept for utilizing fuel cell heat for methane reforming.[5] The system efficiency is estimated to be about 50%. A second UTC design[6] was done as part of a DOE study that Jet Propusion Laboratory (JPL) is coordinating on the subject of coal-based fuel cell plants. In this plant, the excess fuel cell heat is integrated into the gasifier, and desulfurization is done at elevated temperature. The system has an efficiency of 60% HHV. ANL analyzed three natural-gas-fueled plants: 1) high-temperature conventional reforming, 2) sensible-heat reforming, and 3) internal reforming.[7] Efficiencies of better than 50% were found for all three. The relative advantages of each depend on the application. ERC recently finished a more detailed study of a natural-gas-fueled

internally reforming system under EPRI sponsorship. The results of this study should be available soon.

REFERENCES

1. United Technologies Corporation, "Development of Molten Carbonate Fuel Cell Power Plant Technology - Quarterly Technical Report No. 14 for Period January 1, 1983 to March 31, 1983," FCR-5198 (cleared by DOE for publication).

2. General Electric Company, "Development of Molten Carbonate Fuel Cell Power Plant - Quarterly Technical Progress Report for the Period August 1, 1982 to October 31, 1982," DOE/ET/17019-1 (cleared by DOE for publication).

3. Energy Research Corporation, "Development of Molten Carbonate Fuel Cell Technology - Technical Progress Report for the Quarter of January - March 1983," DOE/ET/11304-27 (cleared by DOE for publication).

4. K. M. Parker, "Development of Molten Carbonate Fuel Cell Power Plant - Reference Plant Design Description, Requirements, and Goals," FC-17019-82-14 (September 1982).

5. United Technologies Corporation, "The Study of Integrated Coal-Gasifier Molten Carbonate Fuel Cell Systems," FCR-5208 (July 1983).

6. United Technologies Corporation, "Development of Molten Carbonate Fuel Cell Technology - Quarterly Technical Progress Report No. 7 for Period April 1, 1981 to June 30, 1981," DOE/ET/15440-7 (1981).

7. M. Krumpelt et al., "Advanced Fuel Cell Concepts for the 0.1 to 100 MW Range," Proceedings of the American Power Conference April 1983, Chicago (in press).

SOLID OXIDE FUEL CELLS

D. C. Fee and J. P. Ackerman
Argonne National Laboratory
Argonne, Illinois 60439

INTRODUCTION

Solid Oxide Fuel Cell (SOFC) systems offer significant advantages for a variety of fuels and applications. The simplicity and high efficiency of a direct reforming, contaminant-tolerant power system is advantageous for small natural gas or volatile liquid fueled utility and industrial cogeneration plants, as well as residential use. The further gain in efficiency from the incorporation of a bottoming cycle in large scale plants is advantageous for coal-fueled utility baseload or industrial cogeneration facilities.

Development of SOFC components is well advanced. Materials and fabrication processes have been developed based principally on research at Westinghouse in the United States and Brown, Boveri, and Cie in Germany, along with recent contributions from MITI in Japan and Dornier Systems in Germany. The present effort focuses on improving cell life and performance as well as integration of cells into an array.

COMPONENT DEVELOPMENT

Solid oxide fuel cells have inherent advantages over other fuel cell technologies. The oxide electrolyte is very stable and does not migrate under cell operating conditions. Further, the solid electrolyte and other solid cell components can be fabricated into unique shapes, which cannot be achieved in liquid electrolyte fuel cells. In liquid electrolyte systems, much of the mass and volume goes into fabricating the inert container for the liquid. Eliminating this unnecessary material gives the solid oxide fuel cell potentially unequaled power per unit mass or volume.

Solid oxide fuel cells place stringent requirements on materials. Like other fuel cells, the materials in a solid oxide fuel cell must have the proper: (1) stability in an oxidizing and/or reducing environment, (2) chemical compatibility with the other materials, and (3) conductivity. The materials for solid oxide fuel cells must, in addition, have (4) similar coefficients of thermal expansion (to avoid delamination of the ceramic layers), and (5) compatibility not only at the operating temperature but also at the much higher temperature where the thin layers of ceramic structure are fabricated. For other fuel cells, the components (anode, cathode, electrolyte, interconnection/bipolar plate) can be fabricated separately and then placed together to form a cell. The process conditions for each component can be selected independently. In a solid oxide fuel cell, the process conditions cannot be selected independently for each component. If the thin ceramic layers are built up one by one, the temperature of the sintering operation for each

11

succeeding layer must be lower than the preceding porous
layer to avoid altering the microstructure of the previously-
deposited layer.

The five criteria for cell materials are adequately met
by the present materials selections: strontium-doped
lanthanum manganite for an air electrode, yttria-stabilized
zirconia for an electrolyte, magnesium-doped lanthanum
chromite for the interconnection, a cermet of cobalt or
nickel metal with stabilized zirconia for a fuel electrode,
and calcia-stabilized zirconia for a support tube. (1) The
stability of materials in an oxidizing and/or reducing
environment has been demonstrated in out-of-cell tests over
the range of conditions expected in a SOFC generator. In
particular, an interconnection material has been developed
which is stable in both air and fuel gases. (2) The compat-
ibility of the materials during fabrication and testing
appears to be adequate, based on short-term tests, although
some interaction occurs at the interface of the air electrode
with other cell components. The compatibility of materials
during long-term operation in a SOFC generator (40,000 h or
more) is yet to be determined. (3) The conductivity of the
materials, especially the cathode, could be improved for a
second generation of solid oxide fuel cells. Voltage losses,
due to internal cell resistance, are the principal dissipa-
tive loss mechanism for the ceramic materials and temper-
atures of interest. (4) The thermal expansion behavior of
the cell components has been closely matched by tailoring of
the materials. Cells have been temperature cycled eleven
times (RT to 1000°C in one hour) without loss of performance;
more data are needed, however.

The stability of the fuel electrode appears to be very
good in a high sulfur environment. Sulfur tolerances of
90 vppm for nickel and 200 vppm for cobalt are set, based on
thermodynamic data. (The higher sulfur tolerance of cobalt is
offset to some extent by it lower oxidation resistance.)
Experimentally, approximately 800 h of operation at 50 vppm
hydrogen sulfide have been observed without significant
deleterious effects. Further verification tests of sulfur
tolerance are needed, of course, but it appears the SOFCs
tolerate one to two orders of magnitude more sulfur than
other fuel cells. This simplifies system design by
eliminating the need for desulfurization of natural gas.
Further, the relatively high sulfur tolerance also simplifies
coal gasification/SOFC plants by allowing the utilization of
more energy efficient hot gas cleanup methods. However, the
stability (oxidation resistance) of the fuel electrode could
be improved for a second generation of solid oxide fuel
cells. Improved oxidation resistance of the fuel electrode
would enhance the margin of safety in dealing with non-
uniformities in fuel distribution within a SOFC generator.

The principal thrusts for component development involve
the support tube and air electrode; performance of the
electrolyte and interconnection appear to be satisfactory.

The goal for the support tube is to increase the strength and thermal shock resistance, yet reduce the barrier to gas phase transport. The goal for the air electrode development is to understand the performance tradeoffs arising from the stability, compatibility, conductivity, thermal expansion, and gas phase transport criteria in order to define the appropriate limiting conditions for cell fabrication and operation.

CELL PERFORMANCE

The initial cell performance regularly exceeds present goals. The cell voltage at a current density of 160 mA/cm^2 is approximately 100 mV below the maximum theoretical voltage (outlet Nernst), as shown in Figure 1. This represents an improvement in cell performance of about 20 mV during the last year. However, the total dissipative losses are still large, especially for a high-temperature cell. Further, the dissipative losses impact significantly on cell efficiency because of the unavoidable lower maximum cell efficiency arising from the less favorable thermodynamics of high-temperature operation. The principal voltage loss develops from internal electrical resistance within the cell. In addition, a voltage loss of 10 to 30 mV arises from limitations to gas phase diffusion of oxygen through the pores of the support tube (1 mm thick) and air electrode (0.7 mm thick) to the air electrode/electrolyte interface. Activation overpotentials, as expected for high-temperature operation, appear to be small, within the uncertainty of determinations of cell internal resistance and diffusion overpotentials.

The goal is to increase cell performance through materials selection and/or tailoring of the fabrication processes. Further, the goal is to increase cell life from hundreds of hours, at present, to the thousands of hours necessary for a commercially viable SOFC plant.

SYSTEM PERFORMANCE

Detailed design and development of arrays of cells are underway. The effort focuses on the seal-less generator concept. This design has the advantage that gas tight seals involving ceramics at high temperatures have been eliminated. For example, the spent fuel and spent oxidant streams are separated by a porous barrier of ceramic wool at the outlet of the tubular-shaped cell. The combustion of the spent fuel with the spent oxidant streams occurs on the oxygen-rich side of the porous barrier. The forgiving nature of the leaky seals at the porous barrier minimizes stresses on the ceramic tubes.

The principal thrust of system development involves the fabrication, integration, and control of a generator of the seal-less design. Testing will focus on verifying heat and mass flow as well as mechanical and electrical performance. Some areas, in addition to the cells, are under development.

13

Adequate combustion dynamics in the combustion/preheat chamber and minimal thermal losses through the power contacts have been demonstrated in mock-up tests.

Preliminary systems analyses show the simplicity and high efficiency of this generator design. Efficiencies of nearly 45% HHV are determined for small, direct reforming, natural gas fueled plants without a desulfurization loop or a bottoming cycle. Higher efficiences are obtained with a bottoming cycle or steam cogeneration in natural gas or coal-fueled facilities. Considerable uncertainty exists in these systems analyses, because the electrical and thermal perfor-mance of a SOFC stack have not been demonstrated. However, it appears that Solid Oxide Fuel Cell systems offer signif-icant advantages for a variety of fuels and applications.
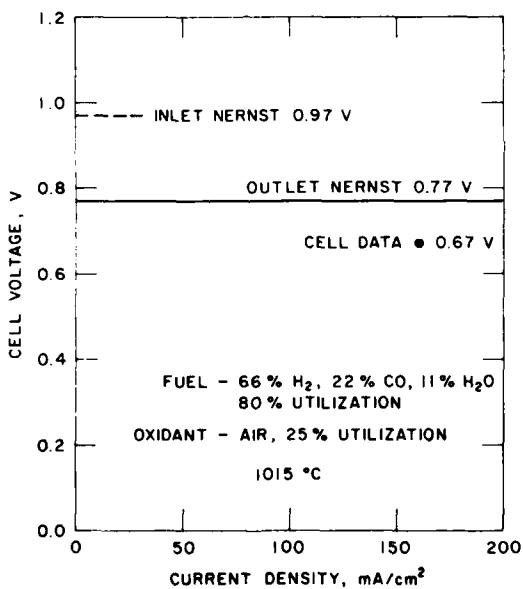
FIGURE 1

SOLID OXIDE FUEL CELL PERFORMANCE

INTEGRATED ENERGY SYSTEMS FOR BUILDINGS*

W. Buchanan, A. Kaufman, S. Pudick,
C. L. Wang, J. Werth, and J. A. Whelan
Engelhard Industries Division
Engelhard Corporation
Menlo Park, Edison, New Jersey

I. Introduction

Engelhard Industries is conducting a fuel cell development program directed toward integrated energy systems for residential and commercial buildings. The main emphasis of this program during 1983 has been improvement and optimization in the areas of cell and stack technology. Other activities include on-going testing and evaluation of a 5kW sub-scale integrated fuel cell power system as well as system, economic, and market analyses for the intended application.

II. Fuel Cell Stack Characteristics

The fuel cell stack technology is based on phosphoric acid electrolyte and forced-circulation dielectric-liquid cooling. Cooling plates are inserted among the cells to establish effective heat-transfer communication between the dielectric liquid and the stack. The nominal operating temperature range is 180-200°C.

A design feature of the stack is an electrolyte replenishment system. This system is tailored to operate automatically, drawing electrolyte from containment that is external to the cells.

III. Stack Component Technology

A key technology activity in the current program involves electrocatalyst development. Advanced formulations are being pursued for both cathode and anode under Engelhard sponsorship. Substantial progress has been made in attaining improved cathode catalyst activity.

In the bipolar plate area, the continuous processing methodology for upgrading low-cost, porous materials with pyrolytic carbon has been verified. In addition, the development of multi-element bipolar plates based on commercial graphite has been reduced to practice in stacks.

The structure of the electrolyte-matrix is specifically tailored to promote the function of the electrolyte-replenishment system. The effectiveness of the matrix structure, in concert with the overall replenishment scheme, has been confirmed over the course of extensive stack testing. The current matrix development program is directed toward minimizing IR-losses.

The technology development effort in the cooling plate area during 1983 has focused on non-metallic structures. Novel configurations have been bench-tested and evaluated in stacks; the most recent trial was in a 4kW stack using two-ft^2 cooling plates. Performance exceeded design goals in all categories except pressure drop.

IV. Application Studies

The main thrust of the system design effort for the building application has been to most effectively integrate the fuel cell power system with the heating, ventilating, and air-conditioning (HVAC) system. This has been supported by economic studies of fuel cell systems in this application.

Economic assessments of on-site fuel cells for residential and commercial buildings were conducted in cooperation with subcontractors, The Trane Company and Arthur D. Little, Inc. Trane has drawn on the economic analysis results in designing HVAC systems for various building applications, while Arthur D. Little has utilized these results in order to forecast the market potential for such fuel cell systems.

Optimization of the fuel cell power system configuration for this application has been carried out with the aid of analytical models provided by subcontractor Physical Sciences Inc. One design objective has been to maximize the fraction of relatively high-grade heat rejected by the fuel cell stack that is made available to the HVAC system. The dielectric liquid stack coolant stream provides good heat-transfer properties, and this would be utilized directly, at a relatively high temperature, in two-stage absorption air-conditioners in the HVAC system, where appropriate.

The results of the economic analyses indicate that, in general, connection of the on-site fuel cell system to the electrical grid is favorable. The optimal sizing of the fuel cell system (relative to the peak electrical load of the building) and design of the HVAC system vary widely, depending on building type and electric (and fuel) rate structure. The building factors that have the largest effect are the ratio of thermal to electrical energy load and the ratio of peak to average electrical load.

16

The figures of merit used in the economic analyses were internal rate of return and net present value (from the point of view of the building owner). These factors, along with other considerations such as building design methodology and ownership, were incorporated into a market penetration model by Arthur D. Little. The results predict that, if fuel cell system cost goals can be met, the building application represents a sizable market for fuel cells.

FIELD TEST - ON-SITE FUEL CELL POWER PLANT PROGRESS

Richard Woods
Gas Research Institute
Chicago, Illinois

Work for this effort was on-going at the time of publication of abstracts.
Papers will be provided to attendess at the Seminar.

ENERGY CONSERVATION BY ON-SITE FUEL CELLS

Hector A. Madariaga, Southern California Gas Company,
for
The Field Test Managers Steering Group

Fuel cell power plants are potentially the best option for on-site supply of building electrical and thermal energy needs. High electrical efficiency combined with recovery of by-product heat provides operating savings for a wide range of building types and climates. Low emissions and minimal noise permit siting at any location. Rapid load response, good electrical power quality, and high part-load efficiency provide an effective energy supply in a wide variety of operating modes.

The natural gas industry, in conjunction with the Gas Research Institute and the U. S. Department of Energy, is pursuing a wide-ranging program to investigate on-site fuel cell power plants in multi-family residential, commercial, and light industrial buildings. The program includes technology development, experimental power plant fabrication, and power plant testing in a variety of applications. Utility input to ensure proper consideration of application factors in the field tests is accomplished through the members of the Field Test Managers Steering Group, identified in Figure 1.

Understanding building energy needs is a significant program element. Buildings require energy for lighting, motors, and appliances; cooling; space heating; hot water; and process needs. These requirements are usually met by a combination of central station-generated electricity and natural gas. The electricity supplies lighting, motors, and vapor compression air conditioning. Natural gas supplies heating, cooking, domestic hot water, absorption air conditioning and process loads.

The on-site fuel cell provides gas utilities with an efficient option for supplying the entire building requirement. Electricity generated at high efficiency by the fuel cell provides the electrical loads. By-product heat from the fuel cell is used to meet a significant portion of the thermal loads. There are a variety of ways in which the on-site fuel cell energy system could be used to satisfy the building needs. Since the energy requirements vary with building type, size, and geographic location, the selection of the most effective system must consider all these factors.

In the on-site fuel cell program, definition of building energy needs through easily usable energy relationships and correlations is being pursued. This activity started with a survey of the annual thermal and electrical energy use and equipment characteristics of nearly 500 buildings. This is being followed with detailed measurement and hourly analysis of thermal and electrical loads in approximately 100 buildings across the United States.

WILLIAM H. BERRY, JR.
CONSUMERS POWER COMPANY

THOMAS A. CLARK
PACIFIC RESOURCES, INC.

EDWARD HOUTS
GEORGIA POWER COMPANY

HECTOR A. MADARIAGA
SOUTHERN CALIFORNIA GAS COMPANY

THOMAS NAPLES
BROOKLYN UNION GAS COMPANY

ROBERT PIASECKI
NATIONAL FUEL GAS DISTRIBUTION CORPORATION

EDWARD A. REID, JR.
COLUMBIA GAS SYSTEMS SERVICE CORPORATION

C. A. ROBERTS
NORTHWEST NATURAL GAS COMPANY

FIGURE 1

Members of Field Test Managers Steering Group

The instrumentation system used in the program is depicted in Figure 2, where the arrows indicate parameters monitored by the Data Acquisition System. These data are recorded on magnetic tape. To ensure proper consideration of seasonal effects, the instrumentation records building energy requirements for a one-year period. Data tapes from the instrumented buildings are analyzed with a computer program that determines the annual building energy use and energy economics for a variety of alternative systems with and without the fuel cell. The analysis is based on hourly energy demand and fuel cell and thermal system performance in meeting that demand. Initially, this analysis is used to select sites for the field test power plants. Subsequently, the analysis is aimed at development of models and correlations that can be used by gas utilities to assess alternative on-site fuel cell energy systems. For field test sites, the monitoring will continue after the fuel cell has been installed to verify these analytical predictions.

At the time this abstract was prepared, 35 percent of the expected site data were available. The current results of the instrumentation and analysis indicate that the fuel cell power plant offers an opportunity for energy and economic savings in a wide range of building types, geographic locations, and application modes. In addition, the results show earlier correlations of energy demand and application results based on monthly billing data are being confirmed by the detailed hourly data.
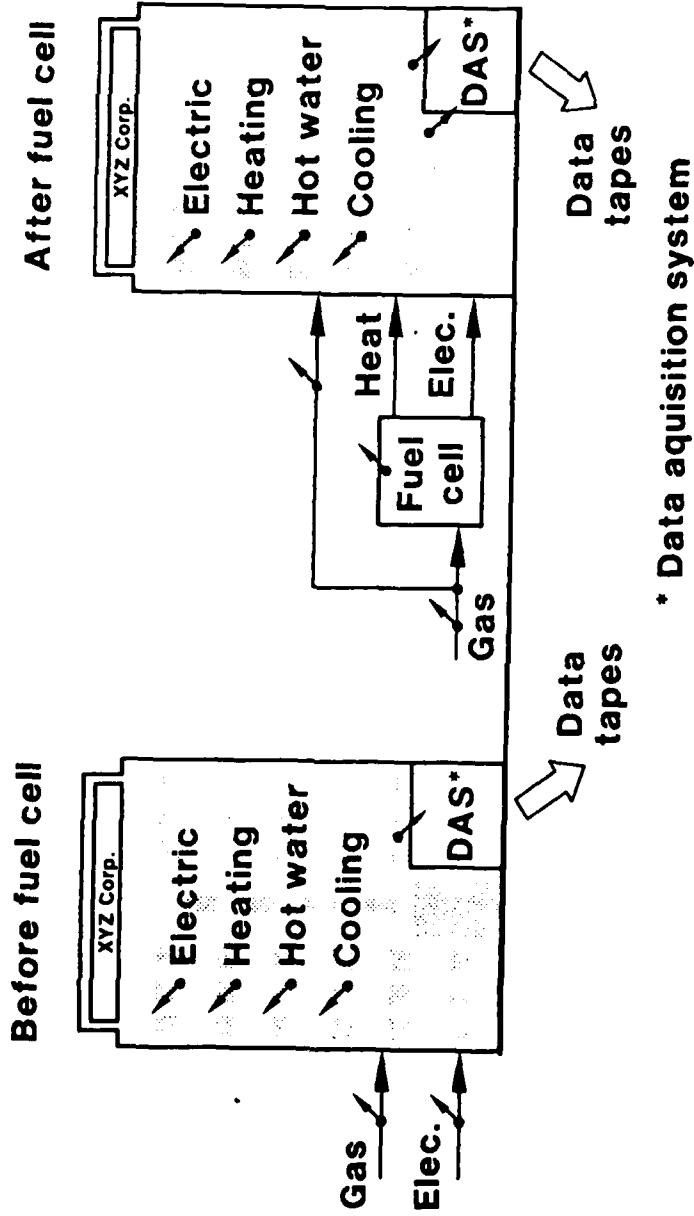
FIGURE 2

Building Data Acquisition System

PROGRESS IN ON-SITE FUEL CELL TECHNOLOGY DEVELOPMENT

Joseph M. King
United Technologies Corporation
P. O. Box 109
South Windsor, CT 06074

In 1981 the Gas Research Institute began the On-Site Technology Development Program, marking a major expansion of the natural gas industry's efforts to bring the benefits of fuel cells to the commercial market place. In keeping with the Government's long-term priorities for efficient utilization of natural resources and a cleaner environment, the Department of Energy joined the program in mid-1982, with efforts managed by the National Aeronautics and Space Administration's Lewis Research Center. This work is being performed in parallel with, and draws upon the knowledge being provided by, the 40-kW Fuel Cell Field Test Program jointly sponsored by the Gas Research Institute and the Department of Energy. The goal of the total program is to advance the knowledge of fuel cell component and systems technology and to identify market applications and business approaches sufficiently for private sector commercialization of on-site fuel cell energy service to begin.

Fuel cell technology has progressed to the stage where complete energy supply systems meeting commercial requirements for automatic operation and economic performance can be provided. The accomplishments of experimental 40-kW power plants have demonstrated this in several early field installations. These machines do not meet commercial requirements for reliability and cost. The primary focus of the Technology Development Program is to correct these deficiencies. The program has three focus areas:

o   Improving the capabilities of basic components--the cell stack, the fuel processor, the inverter.

o   Identifying optimum means for using or adapting industrial components for ancillaries and controls.

o   Identifying power plant design concepts that best match market needs identified by utilities in the Field Test Program.

The fuel cell stack technology goal is a factor of two increase in power density. A series of short development stacks using full-size cells is being used to assess progress in catalysts, materials, cooling techniques and design. Fuel processors with catalyst characteristics permitting increased throughput are being defined. Power processor designs that reduce losses and parts count are being evaluated in brassboard hardware to assess advanced circuit designs and to characterize newly available semiconductors. System design activities address problems uncovered by field test power plant siting and operating experience. These include approaches for correcting reliability problems associated with applying available industrial components to fuel cell systems.

23

BENEFITS OF ONSITE FUEL CELL ENERGY
SERVICE TO UTILITIES AND THEIR CUSTOMERS

Kenneth I. Rapp
Brooklyn Union Gas Company
Brooklyn, New York 11201

The Onsite Fuel Cell Users' Group is a gas industry organization
consisting of gas utility and G.R.I. members who are partici-
pating in the 40 kw - Onsite Fuel Cell Field Test Program. A
significant assignment of the program participants is to conduct
market and business assessment analyses of the role of the fuel
cell in their territories. The analyses are targeted to:
define market and business opportunities; identify barriers and
problems which have to be overcome; and propose actions and
solutions to ensure the entry of fuel cells into commerciali-
zation.

The Fuel Cell Power Plant is a "prime mover" which:

-   is modular and pre-packaged for convenience shipment and
    assembly.
-   has a high electrical generating efficiency.
-   is environmentally benign.
-   provides high efficiency over a wide range of operating
    load conditions and virtually independent of plant power
    rating.

The commercialization of on-site fuel cells provides the gas
industry with opportunities to:

-   add load and revenues through gas sendout.
-   diversify into new energy services business.
-   increase value added to gas sold.

The successful development and commercialization of On-Site Fuel
Cell Power Plants and the energy service business affords the
gas customer opportunities to:

-   meet electrical and thermal energy of his business require-
    ments.
-   lower energy consumption and costs.
-   count on one contractor to supply his energy needs.
-   overcome investment and ownership barriers for advanced,
    upgraded high efficiency energy conversion equipment.

The Fuel Cell Energy Service Business approach affords a
strategy for the gas industry to share in expanded markets and
long term future growth, and to participate in new, higher
earnings, higher return on investment ventures - extending from
the basic core of the marketing, operating and business disci-
plines which most gas utilities already possess.

TECHNO-ECONOMIC EVALUATION OF A DIRECT FUEL CELL SYSTEM

P.S. Patel
Energy Research Corporation
Danbury, Ct.

R. Bharvani   M. Matsumura
Fluor Engineers Inc.   Mitsubishi Electric Corporation
Irvine, CA   Amagasaki Hyogo, Japan

INTRODUCTION

This paper describes an assessment of an efficient, modular and environmentally sound dispersed generator based on internal reforming molten carbonate fuel cell, also called Direct Fuel Cell (DFC). The DFC system processes and consumes fuels such as natural gas within the fuel cell itself, eliminating most of the external fuel processing equipment, associated heat exchangers and other auxiliary equipment, thus promising a low plant capital cost and high reliability. The attractive features of an internal reforming system were also suggested by Krumpelt et al (1) in their study comparing various natural-gas based molten carbonate fuel cell systems. The technology status of this system is discussed in a separate paper at this seminar (2). Due to its simplicity and high efficiency, the DFC system appears quite suitable for many applications, including on-site generation for residential and commercial buildings, industrial cogeneration, dispersed generation as well as large central generators. Results of an evaluation for an on-site application ($\sim$50 kW) presented at the previous National Fuel Cell Seminar indicated that the DFC is potentially a very attractive power generator even in this small size (3). This paper investigates the feasibility of DFC in larger size plants ($\sim$2MW) for dispersed generation, in terms of system configuration selection and parametric analysis, preliminary powerplant design, capital and operating cost estimates, and sensitivity of cost of electricity (COE) to key system design and economic parameters (4). Benefits of incorporating a carbon dioxide exchange device between fuel and oxidant trains have also been examined.

SYSTEM SELECTION AND ANALYSIS

Several conceptual design options suitable for utility application were evaluated with a goal of maximizing electrical generation efficiency. The simplest of the options, operating at atmospheric pressure with an odorant-free natural gas and requiring only one heat exchanger, was selected as the baseline system for parameteric analysis and economic evaluation (Figure 1).

The system efficiency for the baseline system was found to be linear functions of fuel utilization and operating current density. Almost 4 percentage points increase in the system efficiency was observed when the overall fuel utilization was increased from 30% to 90%. A lowering of current density from 200 mA-cm^2 to 100 mA/cm^2 exhibited 5 percentage points gain in the system efficiency, although the fuel cell stack size increased by approximately 75%. A heat rate
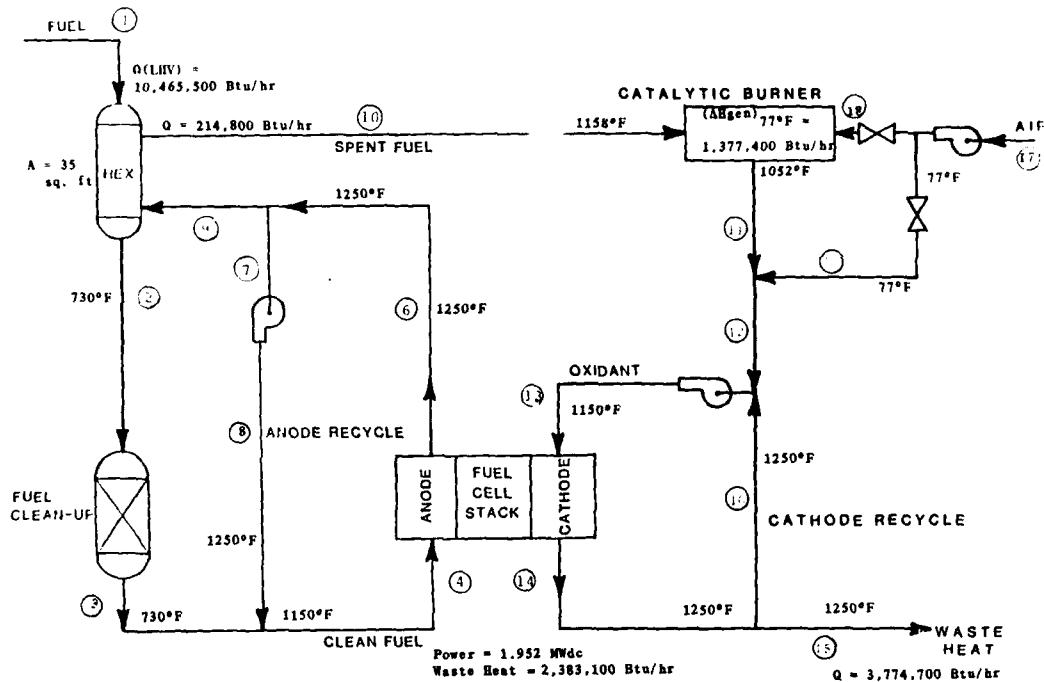
FIGURE 1 - SCHEMATIC OF THE BASELINE DFC SYSTEM

of 6450 Btu(HHV)/kWh was estimated for the baseline system operating at the following set of preferred design parameters:

- 160 mA/cm^2 current density @ 730 mV cell potential
- 90% overall methane utilization (83% per pass)
- 45% recycle for the fuel

PRELIMINARY POWERPLANT DESIGN

Major design specifications for various subsystems were developed with emphasis on utilizing commercially available components. The system is relatively simple, requiring in addition to cell stacks and power conditioner, only one heat exchanger, one fuel clean-up vessel, three blowers, one catalytic burner, and one start-up heater (Figure 2). The layout of the powerplant was based on locating the equipment on four 12x40 ft skids: two fuel cell skids, an auxiliary equipment skid and a power conditioner skid. The shop as-sembled and truck-transportable skids used in the powerplant will minimize construction time and provide a greater ac-cessibility during maintenance. The powerplant will provide a net power of 1.8 MW$_e$ after subtracting auxiliary power and DC to AC conversion losses. The footprint of the powerplant was estimated to be 3400 ft^2.

26

FOOTPRINT
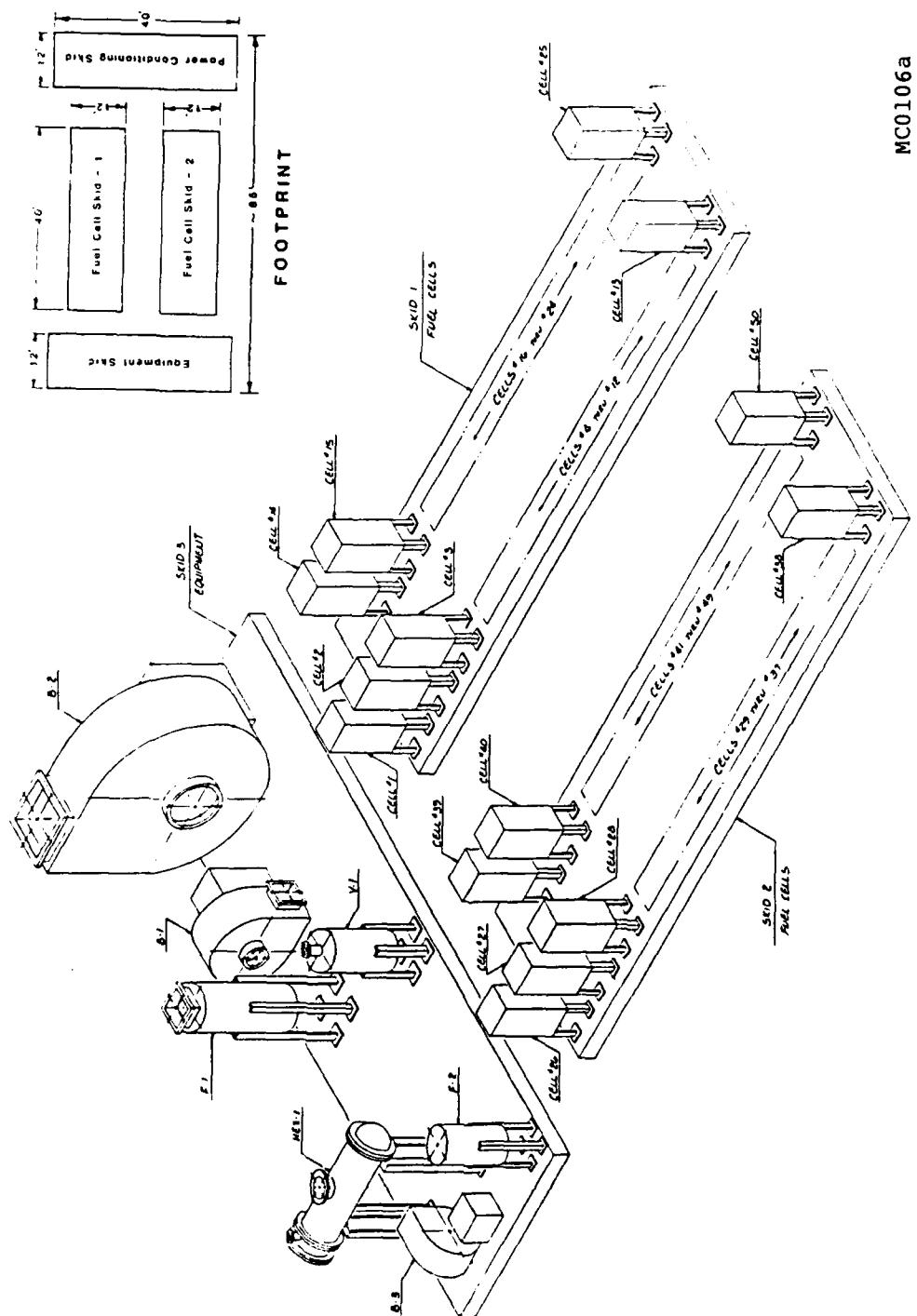
FIGURE 2 - LAYOUT OF THE SKID-MOUNTED 1.8 MW$_e$ DFC POWERPLANT

MC0106a

ECONOMIC EVALUATION

Estimates of capital operating and maintenance costs were developed in constant January 1983 dollars consistent with the EPRI Technical Assessment Guide, Class II level (5). The total capital requirement including total plant investment, organization and start-up costs, working capital and initial change of catalyst was estimated to be approximately $1300 /kW$_e$ (Table 1). The busbar cost of electricity (COE) for the first year of operation (1991) was estimated to be approximately 84 mills/kWh, based on a 90% capacity factor, and a 1983 natural gas cost of $6.13/10^6 Btu(HHV) escalating at a real rate of 3 percent per year. The fuel cost has the major contribution ($\sim$60%) to COE. The contribution from the carrying charges including capital cost is relatively small ($\sim$15%).

Table 1 - INTERNAL REFORMING MOLTEN CARBONATE FUEL CELL POWERPLANT COSTS AND CHARACTERISTICS

(Constant January 1983 $)

Unit Size, Net Electrical Output (100% Capacity), MW$_e$	1.8
Available for Commercial Orders, Year	1991
First Commercial Service, Year	1991
Duty Cycle	Base
Preconstruction and Licensing Lead Time, Years	1-2
Design and Construction Time, Years	<1
Unit Life, Years	30
Heat Rate, Btu/kWh (HHV basis)	6450
Capital Costs, $/kWac	
Total Plant Investment	1230
Start up, Inventory and Land	26
Working Capital	40
Total Capital Requirement in Service	1296
Operating and Maintenance Costs	
Fixed ($/kW-yr)	14
Incremental (90% Capacity Factor)	
Variable including fuel cell	
replacement (mills/kWh)	18.8
Consumables (mills/kWh)	0.6
First Year Cost of Electricity at a fuel price of $7.76/10^{6}Btu(HHV) in 1991 (mills/kWh)	83.7

A sensitivity analysis, carried out to evaluate the relative impact of various design and operating parameters on COE, showed that:

- The natural gas cost and the real escalation rate in its cost has a substantial influence on COE. The first year COF decreased by approximately 7 mills/kWh for a decrease of $1/10^6 Btu in the natural gas price. If the natural gas is assumed to escalate only at the rate of inflation (i.e., 0% real escalation rate rather than the 3% real rate assumed for the baseline), the first year COE reduces from 84 to 73 mills/kWh.

- The fuel cell life has a significant impact on COE for stack life of less than 3 years (Figure 3). The

28

COE decreases by ~30 mills/kWh with an increase in the fuel cell life from 1 to 3 years. However, a further increase from 3 to 5 years results in a further reduction of only 6 mills/kWh. Thus, a fuel life goal of 3 years appears reasonable for an initial market entry.

● Total plant investment (TPI) has a relatively minor effect on the COE: The COE changed only 1 mill/kWh for a $100/kW change in the total plant investment. However, a $100/kW change in the fuel cell stack cost changes the COE by approximately 6 mills/kWh.

This sensivitity analysis therefore provides goals for technology development and also provides guidelines for design trade-off studies.
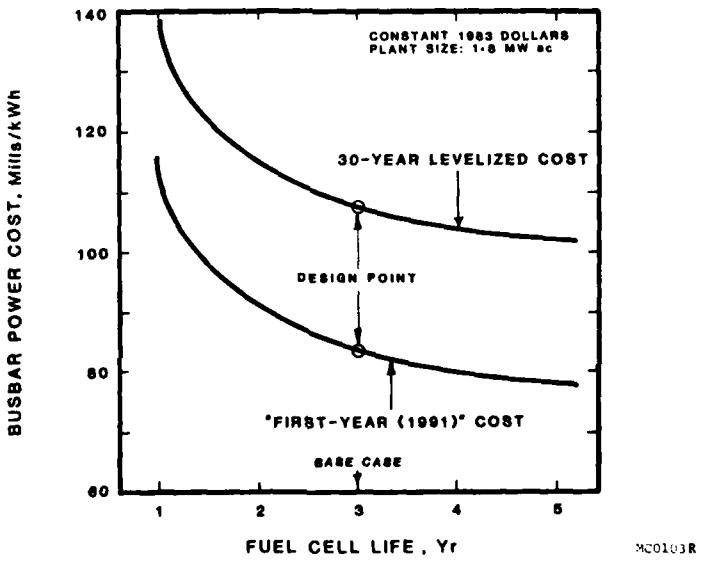
Figure 3 - Effect of Fuel Cell Life on Cost of Electricity

BENEFITS OF A CARBON DIOXIDE TRANSFER DEVICE

The feasibility of a carbon dioxide transfer device (CDTD) was investigated as a further means to improve the efficiency of DFC. Because the above analysis shows that the contribution of fuel cost to COE is five times greater than capital charges, some added capital cost may be justi-fied if it results in an improved efficiency.

A supply of carbon dioxide is required on the cathode side for the electrochemical reaction. On the other hand, a similar quantity of CO_2 is produced on the anode side. The baseline DFC system discussed above provided a transfer of CO_2 from anode to cathode using a burner which converts unreacted H_2 and CO in the anode stream to H_2O and CO_2. The burner exhaust is mixed with the cathode stream to supply CO_2

If the burner is replaced by a CDTD, the unreacted H_2 can be returned to anode and undiluted CO_2 can be fed to cathode. An example of a high temperature CDTD is a $MgO/MgCO_3$ system. Many other CDTD systems are also possible (6).

A preliminary analysis performed to evaluate the benefits of incorporating a CDTD in the baseline system indicated that significant improvements in the fuel cell voltage efficiency and fuel utilization efficiency are conceivable. A CDTD operating in the range of 800-1000°F was incorporated in the baseline system to separate CO_2 from the spent fuel. The unreacted H_2 along with the required amount of steam was recycled back to the anode inlet to achieve a higher overall fuel utilization. Compared to the baseline system, the H_2 partial pressure at the anode exit increased approximately three times. The O_2 and CO_2 partial pressures improved by 30 to 100% depending on the system configuration and the operating conditions. These improvements translated into a 5 to 8% increase in the system efficiency, resulting in approximately 5 mills/kWh savings in the cost of electricity. It appears that a capital cost of approximately $100/kW can be allowed to incorporate a CDTD in the baseline system while maintaining the significant advantage of reduction in COE.

CONCLUSIONS

The natural gas fueled direct fuel cell system appears very attractive as a utility dispersed generator providing a heat rate of approximately 6500 Btu(HHV)/kWh (∿53% efficiency). The system contains a minimal number of components and is therefore very simple and reliable. A total plant investment of $1230/kW$_e$ is estimated for a 2 MW generator which translates into capital charges of ∿12 mills/kWh. Total cost of electricity was estimated to be 84 mills/kWh. Further improvement in heat rate and cost of electricity can be obtained by incorporating a carbon dioxide transfer device.

ACKNOWLEDGEMENT

REFERENCES

1. Krumpelt, M., et al, "Gas Systems", National Fuel Cell Seminar Abstracts, November 1982.

2. Paetsch, L., Pigeaud, A., Maru, H.C., "Component Development for Direct Fuel Cell," National Fuel Cell Seminar Abstracts, November 1983.

3. Patel, P.S., Maru, H.C., and Baker, B.S., "Direct Molten Carbonate Fuel Cell," National Fuel Cell Seminar Abstracts, November 1982.

4. Energy Research Corporation, "A 6500 Btu/kWh Heat
    Rate Dispersed Generator," Final Report prepared for
    EPRI, Contract No. RP1041-12, August 1983.

5. Electric Power Research Institute, "Technical Assessment
    Guide," Report No. P-2410-SR, May 1982.

6. McDonnel Douglas Astronautics Company, California,
    "Study of CO_2 sorbents for Extravehicular Activity,"
    Report Prepared for NASA under Contract No. NAS2-6959,
    Report No. CR114623, July 1973.

COMPONENT DEVELOPMENT FOR DIRECT FUEL CELL

L. Paetsch, A. Pigeaud and H.C. Maru
Energy Research Corporation
3 Great Pasture Road
Danbury, CT 06810

The molten carbonate fuel cell (MCFC) effort at ERC has recently emphasized the development of an internal reforming MCFC, also called Direct Fuel Cell (DFC), wherein carbonaceous fuels such as natural gas and methanol can be utilized directly in the cell, without requiring any external fuel processing to produce a hydrogen-rich fuel. A feasibility analysis of such a powerplant for utility application is described in a separate paper (1) at this seminar. Most of the components for the DFC are similar to a conventional MCFC, except that the anode section should be capable of reforming the carbonaceous fuel to hydrogen, as well as electrochemically oxidizing the hydrogen thus produced. Development of such an anode and an internal reforming catalyst is being pursued at ERC.

Status of the MCFC components was reported in a paper (2) at the 1981 National Fuel Cell Seminar. An update of this paper is presented below, with an added emphasis on natural gas fueled DFC.

ANODE

The recent anode development effort has focused on the improvement in structural strength. A structural degradation of the anode results from both continual sintering and creep deformation of the anode at areas of compressive contact, which increases the contact resistance. The approach taken to improve the structural stability of the nickel based anode is to reinforce the porous structure with low cost, stable ceramic additives, such as lithium aluminate. Initial work with ceramic stabilization focused on impregnation of a presintered nickel anode. Two impregnation techniques were developed: electrochemical impregnation of aluminum hydroxide from aluminum nitrate solution, and direct chemical impregnation of lithium aluminate by precipitation from a potassium aluminate solution. Both of these post-sinter impregnation techniques result in surface coverage of nickel particles with fine ceramic particles, which minimize long term sintering but do not provide adequate creep strength.

A more recent approach to anode stabilization has been to thoroughly mix fine gamma-lithium aluminate with the nickel powder prior to sintering. The metal/ceramic powder mixture is then consolidated by tape casting or mold compression and sintered to produce a stable, creep resistant anode structure. Creep strength has been improved from an 80% deformation for pure nickel to a 5% creep for a nickel+16 wt% lithium aluminate composite anode. Fabrication trials are in progress for direct molding of ribbed structures using this metal/ceramic composite powder. The ceramic reinforced anode has shown good in-cell sinter and creep resistance. Post-test results after 4000 hours of operation showed only minor increases in pore size

(<0.1 µm). Similarly a 60 mil thick ribbed anode decreased by only 2 mils (3.5%) after a 1000 hour test with 60 psi load at contact points.

The anode development work has also included the investigation of a bubble barrier. Experience with thin matrices (20 to 25 mil) has shown a general susceptibility to fracture, particularly during thermal cycles, and hence the use of a bubble barrier is desired for improved cell reliability. Our approach has been to locate a bubble barrier between the anode and matrix where a ductile metallic structure can be maintained in the reducing anode environment. These structures have been fabricated by tape casting of intimately dispersed nickel and lithium aluminate mixtures. Multiple thermal cycle capability and 28 psi bubble pressure have been demonstrated with these structures. The effect of the bubble barrier on cell performance is being investigated.

INTERNAL REFORMING CATALYST

The standard nickel anode does not have sufficient activity to reform all the methane to hydrogen. An adequate reforming capability can be obtained by incorporating an additional reforming catalyst in the anode compartment. This can be achieved by a packed bed of catalyst pellets, as was done in earlier tests at ERC (3), or by catalyzing the bipolar plate or the porous anode itself. In either case a catalyst support, stable in a carbonate environment, is required. Commercially available catalysts use supports such as MgO, Al_2O_3 or $MgAl_2O_4$, which are expected to react with carbonates present in the anode environment. ERC's work has, therefore, been directed at producing catalysts on stable $LiAlO_2$ supports. A variety of catalyst structures suitable for planar geometry of fuel cells have been thus produced. The catalysts with $LiAlO_2$ supports have activity significantly greater than that of a standard nickel anode, and very similar to commercial catalysts, at least at the space velocities of interest for the DFC. Testing of a pellet-type commercial catalyst has demonstrated the initial feasibility of the DFC concept (3). Further testing is being conducted with stable catalyst supports to characterize their activity as a function of carbonate content, temperature and time.

ELECTROLYTE MATRIX

The inert support material for our matrix structures is gamma-lithium aluminate of submicron particle size. Previous emphasis had been on high surface area gamma-lithium aluminate in the range of 15 to 20 m^2/g. Endurance testing, however, showed that the high surface area gradually decayed to approximately 5 m^2/g over several thousand hours. Hence, relatively low surface area material, 3 to 5 m^2/g, is now being employed for matrix fabrication. Present matrix production methods, such as electrophoresis and tape casting, produce a more closely packed support structure than did the previous hot-pressing technology and thus an adequately fine pore size can

now be achieved with relatively low surface area powders. The lithium aluminate is prepared by a simple one-step heat treatment at 1100°C of a stoichiometric mixture of Li_2CO_3 + gamma Al_2O_3. The use of low cost aluminas as starting material is also being pursued.

Two matrix fabrication methods have been developed: electrophoresis (2) and tape casting. Both of these methods are cost effective and suited to full scale production of relatively thin (20 to 25 mil), porous lithium aluminate matrix layers. Electrophoresis involves deposition of lithium aluminate particles suspended in an organic liquid directly on the fuel cell electrodes to produce a uniform, adherent matrix layer. A deposition time of approximately 20 seconds is required to produce a 20 mil matrix and dimensional tolerance of + 1/2 mil is readily achieved. The electrophoretic process has been scaled up to 1500 cm^2 size components and state-of-the-art fuel cell performance has been demonstrated in 300 cm^2 size cells. Improved performance with thin matrix cells results from approximately a 50% reduction in ohmic resistance compared to thicker, conventionally formed tiles. More recently, tape casting has been developed as an alternative approach for an economic production of thin, full scale matrices. Tape casting has an advantage over electrophoresis in that it produces a durable and independent matrix which lends itself to ease in stack assembly and flexibility in cell design. Tape casting involves preparation of a viscous slurry containing the lithium aluminate support powder dispersed in an organic solvent with dissolved binders and plasticizers. The slurry is then cast with a blade over a suitable flat substrate and after solvent evaporation a strong and flexible matrix layer containing a polymeric binder is obtained. The tape casting process is amenable to scale-up and matrices up to 1700 cm^2 size have been fabricated.

Methods to employ the tape matrix in the fuel cell are currently undergoing refinement. The approach being pursued is to burn off the polymers within the cell during initial heat-up at temperatures below the electrolyte melting point (488°C), followed by in situ electrolyte impregnation of the matrix at a higher temperature (500 to 525°C). This in-cell burn out and electrolyte impregnation procedure has been successfully accomplished in laboratory scale fuel cells and high cell performance and thermal cyclability have been demonstrated with tape matrices. Some initial difficulties associated with tape burn out and shrinkage were encountered in bench scale cell testing. However, solutions have now been obtained and testing is in progress. At the present time both tape casting and electrophoresis are under evaluation and final selection of the preferred fabrication method will be based on manufacturability and cost considerations.

CATHODE

Nickel oxide has been used as the standard cathode material so far, but some concern has been raised about its

solubility in the cathode environment and subsequent nickel re-
precipitation in the matrix. ERC's approach to understanding
and solving this potential problem is twofold:

1.   Investigate the effect of different electrolytes and op-
      erating conditions on NiO solubility and devise approaches
      to ensure stable long term operation of cells built with
      nickel oxide cathodes, and

2.   Investigate alternative cathode materials in cooperation
      with Westinghouse Corporation.

Effort has been initiated on both of these approaches. The em-
phasis in alternate cathode materials will be placed on mate-
rials that do not require significant changes in other cell
components. The materials already prepared and characterized
by Westinghouse for solid oxide fuel cells are being screened
for their possible compatibility with MCFC and several candi-
date materials are presently being tested in the MCFC cathode
environment.

CELL HARDWARE

      Stackable bipolar plates between the individual cells of a
multicell stack have been considered in a variety of configura-
tions. In addition to its normal functions, there is now also
the requirement of internal reforming in the anode chamber.
The catalyst placement and changes in gas flow distribution,
depending on the ongoing studies, may result in some bipolar
plate modifications. Fabrication trials of sheet metal bi-
polar plates have confirmed the feasibility of various folding
and welding steps, as well as the application of protective
coatings.

      Single cell hardware has been improved steadily to provide
a reliable test vehicle. These improvements include the use of
Inconel-600 anode current collector and nickel coating of the
anode housing.

CELL TESTING

      Testing in 10 and 300 cm^2 size cells has been conducted
to evaluate the various components described above. Several
DFC's have been operated with different loadings (20 to 100
mg_{Ni}/cm^2) and arrangements of internal reforming catalysts for
periods ranging from 500 to 3000 hours. The performance level
of these cells with a direct methane feed was found to be
equivalent to that expected from prereformed methane fuel.

      The internal reforming capability in a 300 cm^2 size DFC
with a loading of 100 mg_{Ni}/cm^2 as a function of time and elec-
trolyte addition is shown in Figure 1. A complete methane con-
version to hydrogen was observed at a 50% H_2 utilization and
115 mA/cm^2 current density for over 1700 hours. A decline in
catalyst activity was observed beyond this point, which may be
caused by the excessive electrolyte addition as shown in the

35

figure. Post test analyses of the catalyst in this cell showed
a significant level of carbonate in the catalyst and reaction
of the MgO-Al$_2$O$_3$ based catalyst support. The need for develop-
ment of a stable catalyst support and the importance of mini-
mizing the exposure to electrolyte is indicated in this test-
ing.
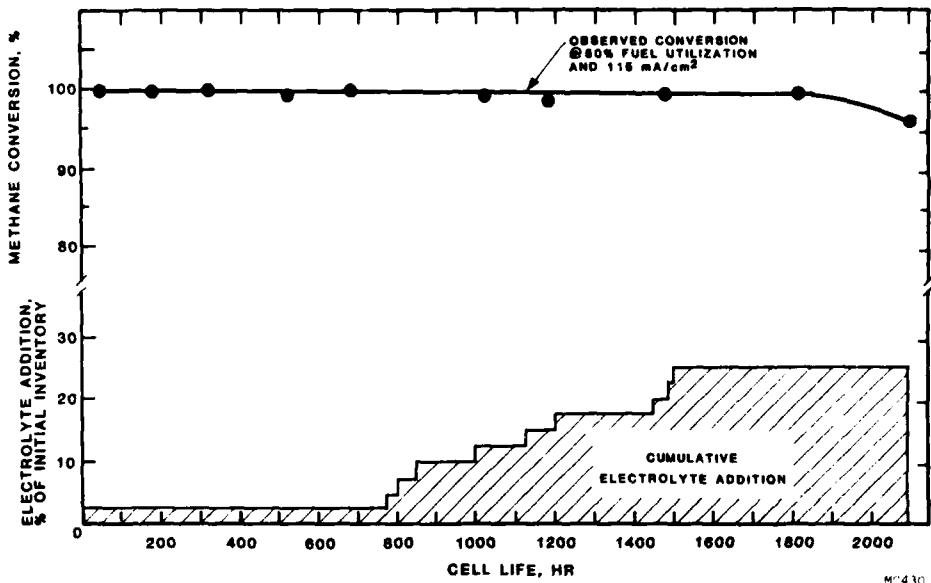
FIGURE 1.   INTERNAL REFORMING PERFORMANCE OF A
300 cm^2 SIZE DFC AS A FUNCTION OF
TIME AND ELECTROLYTE ADDITION

The present average operating temperature of 650°C has
been arrived at primarily from the considerations of initial
performance. Recognizing that the cell temperature is also an
important variable in the stability of cell and stack compo-
nents, an effort has been initiated to investigate the feasi-
bility of a lower temperature operation. A detailed investi-
gation has revealed that by a modest lowering of the tempera-
ture (approximately 35°C), it is possible to significantly re-
duce the corrosion, anode creep, electrolyte loss and cathode
instability. Cell performance loss associated with the low-
ering of temperature may be minimized by some minor readjust-
ments in cell components. Several cells have been operated
with a stable performance at 615°C for up to 3000 hours. Com-
ponents from these cells will be analyzed to compare their
structural stability with standard cells operated at 650°C.

ACKNOWLEDGEMENTS

REFERENCES

1. Patel, P.S., Bharvani, R., and Matsumura, M., "Technoeconomic Evaluation of a Direct Fuel Cell System," National Fuel Cell Seminar Abstracts, November 1983.

2. Maru, H.C., Pigeaud, A., and Paetsch, L., "Progress in Molten Carbonate Fuel Cell Components Technology," National Fuel Cell Seminar Abstracts, June 1981.

3. Patel, P.S., Maru, H.C., and Baker, B.S., "Direct Molten Carbonate Fuel Cell," National Fuel Cell Seminar Abstracts, November 1982.

STATUS OF MOLTEN CARBONATE
FUEL CELL DEVELOPMENT AT UNITED TECHNOLOGIES CORPORATION

A. P. Meyer, C. A. Reiser, H. R. Kunz, C. R. Schroll
United Technologies Corporation
Fuel Cell Operations
South Windsor, CT 06074

The Molten Carbonate development effort at UTC during the past year has focused on elimination of the performance degradation associated with electrolyte migration and finding an alternative cathode catalyst material to nickel oxide, which is not stable at elevated operating pressures. This work has been carried out under a group of complementary programs sponsored by the U.S. Department of Energy, the Electric Power Research Institute, the Gas Research Institute, the Niagara Mohawk Power Corporation and United Technologies.

Electrolyte Migration Investigation

Two major electrolyte transport paths have been identified and investigated. One transport path is from the matrix of an individual cell through the cell's edge seal to the outer surface of the cell. The second is migration perpendicular to the cell plane through the manifold gaskets.

Figure 1 illustrates the mechanism which causes electrolyte migration through the seal region. The outer surface of the anode gas housing acts as a cathode where carbonate ions are produced. Potassium and lithium ions migrate through the seal to provide charge neutrality. Other mechanisms then transport electrolyte away from the site. The continuing process causes the cell to lose electrolyte or to "dry out".
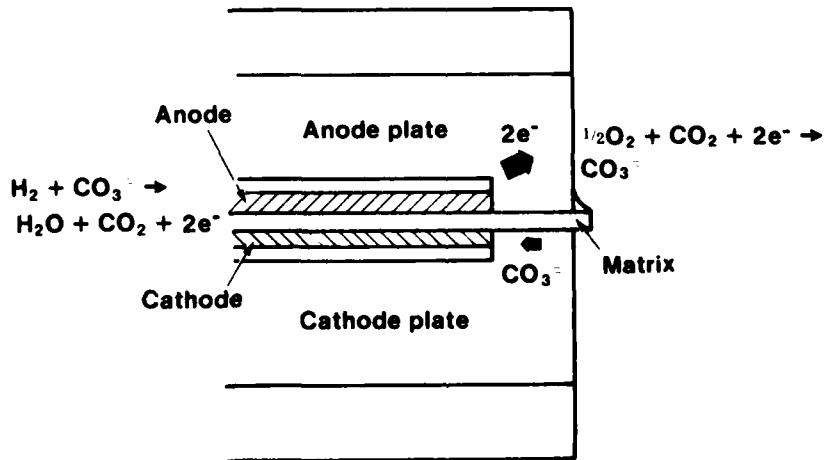
FIGURE 1   SCHEMATIC DRAWING OF ELECTROLYTE LEAKAGE

Single cells incorporating changes to reduce migration have been tested. The results are shown in Table 1. This data compares the electrolyte inventory of modified cells after 2000 hours of operation to that of a typical conventional cell. The modified cells show a significant decrease in electrolyte loss.

TABLE 1

SUMMARY OF SINGLE-CELL ELECTROLYTE
INVENTORY ANALYSES

Inventory as Percent of Fill

Cell	$LiCO_3$	K_2CO_3	Remarks
A	58	89	Conventional cell
B	86	97	Modified design
C	98	95	Modified design
D	85	100	Modified design
E	92	96	Modified design

With respect to the second major transport mechanism, migration perpendicular to the cell plane through the manifold gaskets, analysis and corroborating tests have shown that migration rate along this path is a function of gasket material properties. The test apparatus shown in Figure 2 is being used to establish the relationship between electrolyte transport and seal properties. Gaskets of different configurations and with different properties are clamped between the two alumina plates and subjected to stack conditions of temperature and potential. Resultant electrolyte migration and changes in gasket electrolyte content are determined by measuring ionic flow and electronic resistance of the gasket along its length.

The design modifications that have been defined based on single-cell tests and alternative manifold gasket configuration being defined by the work now in progress, will be evaluated in a 20-cell stack of one-foot square cells during the fall of this year.
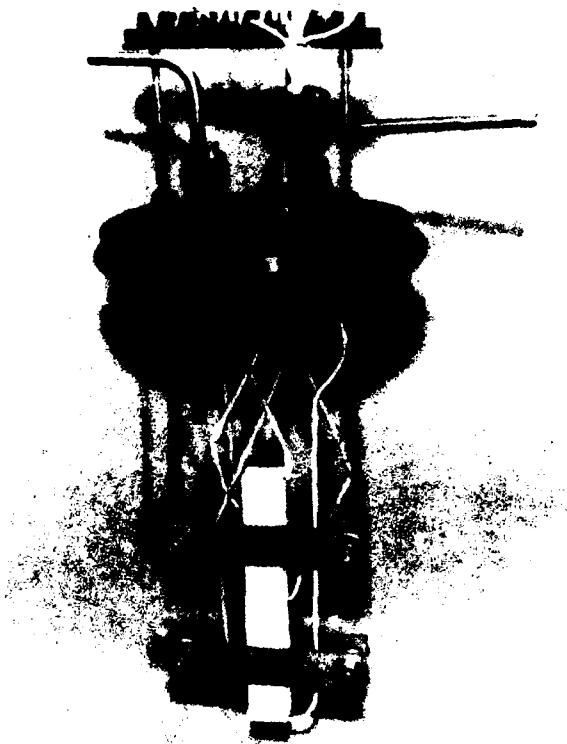
FIGURE 2   TEST RIG FOR MEASURING ELECTROLYTE MIGRATION

Alternative Cathode Catalyst Development

The objective of this work is to produce a cost-effective alternative cathode catalyst material for use at elevated operating pressures.   Several materials are being investigated.   Lanthanum cobaltate when screened initially in out-of-cell tests looked promising.   Subsequent single-cell tests showed it to be unstable at operating potential. Modifiers to stabilize the material at potential are being considered.   Tests to date show lanthanum ferrate to be stable at all conditions including those of operating potential.   However, its electronic conductivity is low. Means to improve its conductivity are being evaluated.

STATUS OF MOLTEN CARBONATE FUEL CELL PROGRAM AT GENERAL ELECTRIC

R. W. Barta
General Electric Company
Ballston Spa, New York

Work for this effort was on-going at the time of publication of abstracts.
Papers will be provided to attendees at the Seminar.

STABLE MATERIALS FOR MOLTEN CARBONATE FUEL CELL CATHODES

J. L. Smith, T. D. Kaun, N. Q. Minh, and R. D. Pierce
Argonne National Laboratory
Argonne, Illinois 60439

Introduction

Work on an alternative to nickel oxide as the cathode material for the molten carbonate fuel cell has been underway for about 1-1/2 years. During that time, the procedures have evolved significantly from the initial approach of surveying the literature for conductive, possibly stable, compounds. Current emphasis is on compound stability with the result that most of the compounds of interest are new to the literature on conductive ceramics. In the current phase, applied testing is being emphasized to screen unsuitable materials more rapidly than would be possible with more fundamental measurements (i.e., conductivity, solubility, etc.).

Experimental

In developing stable cathode materials, the first step is to choose the cations on which to base the stable materials. A major factor for a commercial endeavor is cost and availability. Technically, it is important to choose a transition metal in order to induce conductivity by doping. And, finally, only cations were chosen that will not reduce to metal in anode conditions. This criterion was chosen to reduce or eliminate the sink for cathode ions near the anode. By reducing the sink term, a larger source (i.e., higher solubility in the cathode environment) can be tolerated.

With these criteria in mind, a number of cations were chosen for synthesizing stable materials. Determination of stable compounds at cathode inlet conditions was done by exposing oxides of the chosen cations in powdered form to excess eutectic in cathode gas (28% CO_2, 14.5% O_2, 57.5% N_2) at 650-700°C for 100 h. The products of reaction were washed, then analyzed by X-ray diffraction. Results of this test are shown in Table 1. In most cases, there is little or no information available on conductive forms of these compounds. Doping studies on certain of these compounds were then initiated.

Several detailed procedures were used for preparing the materials, but in general a homogeneous mixed oxide of the dopant/parent cations was produced. This product was then reacted in the cathode environment to produce a stable doped compound. The stable materials thus formed were washed, pressed into pellets, and sintered (typically 1 h @ 1300°C). These procedures avoid lithium-loss problems during inter-diffusion and produce an inherently stable material.

After synthesizing doped stable materials and sintering pellets, conductivity is tested using the van der Pauw method. A temperature range of up to ~750°C is normally used. All testing is done in air. The van der Pauw

measurement is good only for electronic conductivity. On some pellets, a qualitative test examining ac phase shift was done.

The production of stable conductive materials provides only a starting point for the cathode development effort. There must also be a series of screening tests including further stability tests, solubility tests, and cell tests. At the outset of the program, the dopant tests were performed first to look at the feasibility of inducing conductivity in the stable material. These are very time-consuming tests, and the present policy is to do the initial screening by other means. A "migration" test has been initiated for this purpose. This is a cell test run with an undoped cathode. It is intended to be a pragmatic solubility test which looks at the effect of solubility in both the anode and cathode environments. The test evaluation is exclusively by posttest examination for the cations of the cathode material. This is complemented by more fundamental solubility tests, both pot-test and cyclic-voltammetry tests. Further stability tests are also being run. Oxides of the candidate transition metals are exposed to excess carbonates and a range of cathode gases. For a material to be a viable candidate, it should be stable under all probable cathode conditions.

In addition to the materials development, a generic cathode fabrication development is being initiated in order to have the capability of fabricating structures with appropriate pore characteristics from the variety of materials that will be used in cell tests.

Results

The results of the tests described will be discussed. Currently, based on conductivity, stability, and migration tests, Li_2MnO_3, $LiFeO_2$, and ZnO look promising. Table 2 shows typical resistivities for these compounds with selected dopants. ZnO has been examined for lithium poisoning, with positive results to date, but tests are continuing to evaluate this concern.

Li_2MnO_3 doped with Mg has a resistivity of less than 5 $\Omega \cdot cm$ in a 40-50% porous body at 650°C in air. There is a single stable compound in the gas compositions tested to date. The solubility is very low, which agrees with a preliminary migration test.

$LiFeO_2$ doped with Mn also has a resistivity of less than 5 $\Omega \cdot cm$ for a 40-50% porous body at 650°C in air. There is also a single stable compound. The solubility appears comparable to that of NiO under dry conditions and lower under humid conditions. An initial migration test indicated that the migration and deposition problem may not exist for this compound.

43

ZnO has excellent conductivity and is stable not only in all cathode conditions but also in anode conditions. Conductivity will be poisoned if the compound is doped in-situ with lithium. The extent of doping of this material in the cathode environment is currently being examined.

Table 1. Stability of Alternate Cathode Materials in an Inlet and an Exhaust Gas Environment at 700°C in Excess Li_2CO_3-K_2CO_3 Eutectic.

Exhaust Gas	Inlet Gas
CO_2 = 3.4%, O_2 = 14.6% N_2 = 76.7%, H_2O = 5.3%	CO_2 = 28%, O_2 = 14.5% N_2 = 57.5%
Li_2MnO_3	Li_2MnO_3
Li_2TiO_3	Li_2TiO_3
Li_3TaO_4	Li_3TaO_4
MgO	MgO
K_2WOP_4	K_2WO_4
ZnO	ZnO
Li_3VO_4	Li_3VO_4
Li_2SnO_3	Li_2SnO_3
α-$LiFeO_2$	α-$LiFeO_2$
Li_2ZrO_3	ZrO_2

Table 2.   Resistivity of Some Stable Doped Compounds in Air.

Stable Compound	Dopant	Resistivity at 650°C
Li_2MnO_3	Mg	5 $\Omega \cdot cm$
	Zn	50
	Al	100
$LiFeO_2$	Mn	5
	Mg	500
	Zn	600
ZnO	Cr	2
	Zr	3
	Al	10

MOLTEN CARBONATE FUEL CELL COMPONENT DEVELOPMENT

E. H. Camara and E. T Ong
Institute of Gas Technology
3424 South State Street
Chicago, Illinois   60616

Introduction

During the past year, under the sponsorship of the Electric Power Research Institute (RP-1085-2), IGT has been developing advanced components for molten carbonate fuel cells. Our research efforts were dedicated to the —

- Development of copper base anodes as an alternate to the baseline stabilized nickel anodes

- Evaluation of copper-clad stainless steels for use as separator plate material

- Optimization of tape casting for production of electrolyte matrices and,

- Evaluation of catalysts for internal reforming molten carbonate fuel cells.

The most relevant results of our research are presented below.

Development and Evaluation of Copper Components for MCFC

Copper possesses a number of chemical and physical properties that make it an attractive choice for use under anodic conditions in molten carbonate fuel cells —

- Copper's superior resistance to anodic oxidation (~290 mV more noble than nickel) permits operating stacks at higher current densities.

- Copper is expected to offer superior resistance to carbon transport from the fuel gas into the separator plate, which can result in carburization and embrittlement of the stainless steel portion.

- Copper has a significantly higher electrical conductivity than nickel.

- Copper's higher thermal conductivity relative to nickel provides improved capability for cooling the stack during operation.

- Copper has a better match in coefficient of thermal expansion with other cell materials (austenitic stainless steel, electrolyte tile), reducing the level of thermally induced cell stresses.

In addition —

46

- The use of copper as a substitute for nickel in the anode offers the potential for an approximately two-fold decrease in the cost of the raw powder material.

- The United States is much less dependent on foreign sources for copper than for nickel.

IGT has developed low cost fabrication techniques to manufacture copper anodes with microstructure comparable to that of the baseline Ni = 10% Cr, as shown in Figure 1. Large 6-in. x 6-in. plaques have been routinely obtained by low pressure sintering of pre-reduced CuO powder.
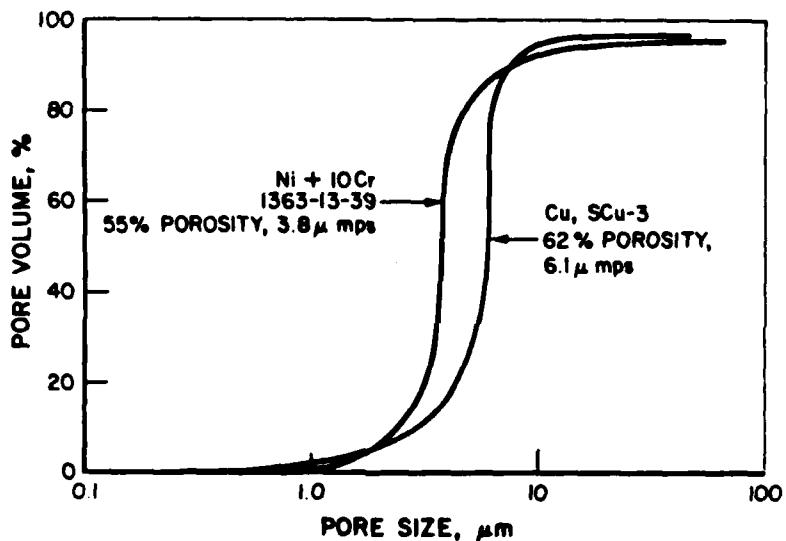
Figure 1. POROSIMETRY OF A Ni + 10% Cr ANODE AND
A Cu ANODE FABRICATED BY LOW PRESSURE SINTERING

Tape casting has been shown to be a more practical fabrication technique because it can also be used to manufacture other cell components and it also produces a more uniform microstructure than dry powder sintering. This process, however, has not been fully developed to routinely produce electrodes.

IGT has demonstrated the feasibility of using copper anodes in molten carbonate fuel cell tests. Electrochemical half-cell studies showed that the electrocatalytic activity for H_2 oxidation is comparable to that of nickel. Tests using stabilized porous copper anodes in laboratory scale (3-cm^2) fuel cells indicated comparable initial performances as the baseline stabilized nickel anode, as shown in Figure 2. However, bench-scale cell tests have identified as major

problems, creep deformation and particle sintering of the copper anodes at operating temperature and stack holding pressures. Sintering can be controlled, but our experience indicates that reinforcement is needed even with particle stabilized copper anodes to provide for load distribution to reduce local deformations and creep.
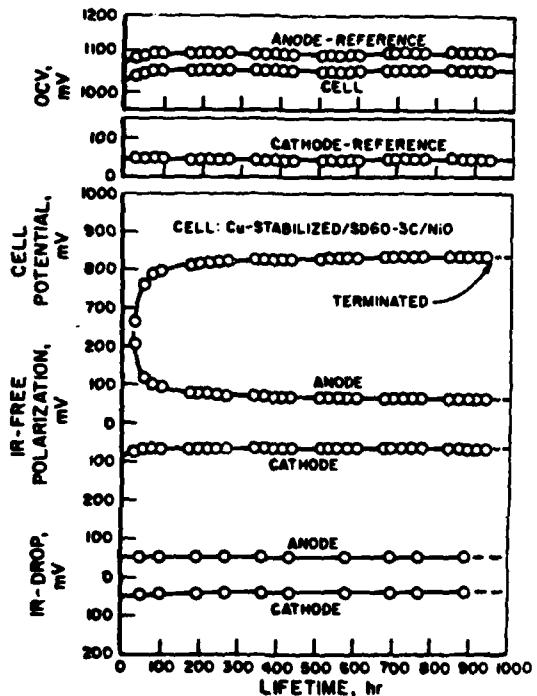
Figure 2. LIFETIME PERFORMANCE PLOT OF
CELL RD-1 (3-cm^2) USING
STABILIZED Cu ANODE

Another use for copper in MCFC is in the bi-metallic separator plate, where the copper side faces the anode and the stainless steel faces the cathode. Nickel has been previously used with good success. Stainless steel/copper clad 10 mil thick formed sheets have been tested in bench-scale fuel cells with stabilized copper anodes for coating quality and chemical stability against corrosion under cell operating environments. Results demonstrate the potential of copper-clad stainless steel sheets for fabrication of separator plates; however, the anode wet-seal area still needs to be coated for protection.

Optimization of Tape Casting for Production of Electrolyte Matrices

The objective of this effort is to optimize IGT's tape casting process for large-scale production of electrolyte

matrices. The process involves uniformly dispersing the electrolyte powder in an organic vehicle to form a slurry which is then continuously cast on a smooth substrate, a moving doctor-blade controlling the thickness of the casting. Final processing involves heating (in- and/or out-of-cell) at a controlled rate to remove the organic vehicle constituents.

Tape casting parameters have been systematically varied to optimize such factors as vehicle formulation, powder/vehicle ratio, casting thickness, and binder burnout/impregnation schedules. Tape cast structures have been characterized with respect to density, thickness, uniformity, and microstructural homogeneity. They have also been evaluated in bench-scale cells for performance with stabilized nickel anodes, in-situ oxidized nickel oxide cathodes, and bubble barriers. Results from these cells (Cell BS-TC-3 performance results shown in Figure 3) indicate that the power output goal is achieved, as the cells yield 780 to 800 mV at 160 ASF (fuel containing 60% H_2 + 40% CO_2, 140°F dew point, 75% utilization; oxidant containing 70% air + 30% CO_2, 140°F dew point, 50% utilization) for ~300 hours. However, after 300 hours of operation, the decay rate is unacceptable. This decay is attributed to carbonate losses caused by changes in the $LiAlO_2$ microstructure. We are presently modifying our initial $LiAlO_2$, produced from low-cost aluminas, to control the microstructural changes and the electrolyte losses.
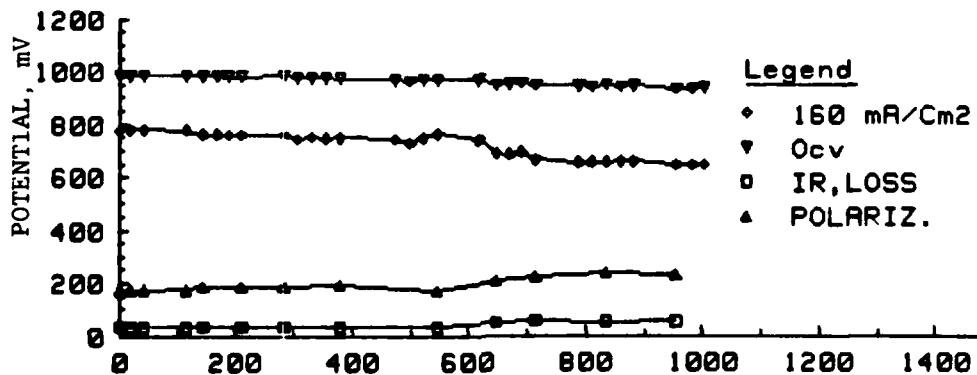
Figure 3. LIFEGRAPH OF CELL BS-TC-3

Evaluation of Catalysts for Internal Reforming MCFC

The objective of this effort is to determine the performance and endurance characteristics of internal methane-reforming catalysts which are potentially resistant to the carbonate environment. Catalysts developed under an IGT-sponsored program, as well as catalysts on new support

materials, are being examined. Presently, evaluations are being conducted out-of-cell, in tubular reactors. When suitable catalyst/support combinations are identified, they will be tested in tape matrix cells.

Figure 4 presents the initial evaluation of an IGT catalyst. These results, obtained under conditions used in commercial steam reforming operations for hydrogen production, indicate that methane conversion is hindered by carbonate contents greater than 5%. However, the testing conditions are much more severe than conditions prevailing in the fuel cell anode, and we expect significantly improved catalyst performance under cell conditions.
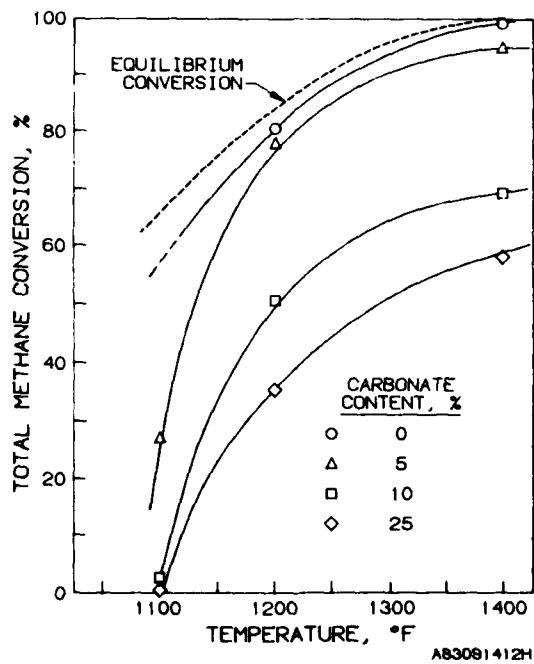
Figure 4. EFFECT OF CARBONATE CONTENT ON
THE STEAM-METHANE REFORMING REACTION
AT 1-ATM, 1400 HR^{-1}, AND H_2/CH_4
RATIO OF 2.5/1

Acknowledgment

4.8-MEGAWATT DEMONSTRATOR: A PROGRESS REPORT

Leonard Gelfond
Consolidated Edison Co.
New York, New York

At the presentation last year, we had just completed modification and repair of the reformer and replacement of the steam/glycol heat exchanger. The process and control (PAC) test was officially re-started on November 14, 1982 and completed June 17, 1983. The purpose of the PAC test was to verify the operating condition of the dc module, control system, and auxiliaries prior to installation of the cell stacks.

The sequence of events described in this presentation started with determination of water quality in the water treatment and thermal management systems and continued through operation of the fuel processing system including hydrogen production and simulated load.

The Water Treatment System (WTS) and Thermal Management System (TMS) were operated together to reduce the conductivity and turbidity of stored water to acceptable levels. To hasten the clean-up process, demineralized water was brought in by truck and filters were added. A water polisher is being added to the dc module to further improve quality.

The Fuel Processing System (FPS) and Hydrodesulfurizer System (HDS) were started November 30, 1982. Early testing indicated no change in the control settings since March 1982 when testing was interrupted by the reformer problem reported last year. The process continued with a smooth light-off of the new reformer gas torches on the first attempt. After a few more start-ups, high flow turbocompressor (HFTC) surge shutdowns were encountered. Evaluation of the HFTC performance indicated a significant reduction in effective area at the hot gas inlet from the auxiliary burner. The HFTC was removed, damage to the auxiliary burner liner was seen, and liner pieces were removed from the HFTC. A more detailed examination of the HFTC indicated damage to both rotor and stator.

Examination of removed sections of the damaged liner indicated the failure had been caused by high frequency oscillations in the gas stream. A new liner of a smaller diameter was fabricated and installed along with a baffle to reduce or eliminate the vibration. During this period, the HFTC was repaired. Two months were required from the appearance of the problem to the completion of repairs and resumption of testing.

Efforts to continue the PAC test were interrupted by the discovery of a weld crack in the 14-inch TMS exhaust pipe and at the inlet duct connected to HEX 411 on the other end of the 14-inch pipe. Investigation revealed a thermal stress problem. Repairs to the TMS were performed and an expansion joint added to prevent any future damage. While the repairs were in progress, large carbon deposits were found in the TMS burner. These were subsequently determined to result from inadequate primary air. Although the TMS burner is rated at 5,000,000 BTU per hour, the maximum allowable heat delivery was held to 3,000,000 BTU per hour by a limitation in the TMS burner blower. This will be

temporarily remedied by adding electrical heaters.

After several more tests, inspection of the new auxiliary burner revealed localized buckling and eros¨on. Analysis of the data indicated the baffle, which was installed over the by-pass air inlet to reduce high frequency vibration, was causing eddies and low pressure pockets resulting in auxiliary burner flame distortion. The air/fuel ratio was adjusted to reduce flame temperature. After several test starts, inspection of the liner revealed temperature in the hot area was acceptable.

In early 1983, approximately two weeks after the TMS burner was repaired, operation to the point of transition to fuel and steam in the reformer became repeatable. Since then, the sequence of events to completion of the PAC test was:

March 30	Produced hydrogen
April 13	Transitioned reformer to process gas
April 14	Transitioned auxiliary burner to process gas and reached standby
April 15	Reached a stable standby condition
May 13	Ran simulated 25% load for 3 minutes
June 8	Ran simulated load for 52 minutes
June 13	Verified standby-to-load transition
June 14	Transitioned TMS burner to process gas
June 16	Reached standby with transitioned TMS burner and manually shut down via emergency mode
June 17	Completed PAC test

The 52-minute period at simulated load reflected optimized process gas/steam control adjustments. With the PAC test configuration, the steam supply is marginal and the TMS burner cannot maintain the water temperature when cold make-up water is introduced. During normal operation with heat supplied by the cell stacks, this will not be such a problem. Because of this condition, the objective of demonstrating two hours of simulated load was abandoned as unrealistic for the PAC test configuration.

Before the acceptance test can be run, minor changes to valves, controls, ADAR, etc. will be made, and the equipment will be modified as follows:

1. Install power section pallets
2. Add water polishing loop
3. Install cell stack coolant line blinds
4. Install turbocompressor inlet duct
5. Incorporate PAC heater permanently into TMS
6. Install anode by-pass

7. Install HEX 317 by-pass

Meanwhile, Power Conditioning System (PCS) testing had been carried on in parallel with PAC testing. PCS testing was completed in March, 1983. Difficulties were encountered resulting from extraneous signals in the switching logic. These were corrected by modifying the gate-drive logic and improving the grounding and shielding of the gate-drive cables. This allowed completion of the line parallel test for zero VAR output. Additional control stability problems were corrected by substitution of larger sized inductors. This change allowed stable operation at $\pm$ 4.5 MVAR, the full rating. Functional tests and a 95-hour thermal stability test were successfully completed. Discussions by an EPRI/Con Edison PCS committee led to a decision to conduct a 100-hour operational test of the PCS operated from the site controller.

PAC Test Observations

1. Once hardware and controls are set, start-ups were generally repeatable.

2. The limitations of the TMS burner and a greater heat loss than expected resulted in a start-up time of 9-10 hours from a cold condition and 5-6 hours from a hot condition.

3. Investigation and resolution of problems would be facilitated by improved component accessibility.

4. More provisions for isolation of pipe sections would be useful.

5. Additional filtration was added because of rust particles in piping. In the future, hydrotesting of piping should be strictly avoided. If this is not possible, piping should be stainless steel to minimize corrosion.

6. Verification that the naphtha and stored water meet their specifications is time consuming.

7. An enclosure for freeze protection and maintenance is recommended for installations in areas such as New York. A temporary enclosure may be considered as an alternative.

8. Freeze protection measures for instrumentation should be improved.

9. Air and nitrogen leakage was greater than anticipated.

10. All valves should have visual position indication.

11. With the present turbocompressor silencer arrangement, compressor inlet air is heated by the turbine exhaust ducting, reducing the allowable ambient temperature for full-power operation. The intake is being reconfigured.

12. Automatic operation of the WTS, cooling towers, and dc module has not yet been fully demonstrated.

53

13. Hot spots were noted on the outside of the reformer vessel. They are attributed to slippage of the internal insulation. Future designs should correct this situation.

14. During initial start-up more consideration could be given in software design for non-standard conditions.

15. Start-ups would be easier if there were greater manual control of some functions.

54

4.5 MW FUEL CELL POWER PLANT TEST AT TOKYO ELECTRIC POWER COMPANY

Michio Kobayashi
Engineering Research and Development Center
The Tokyo Electric Power Co., Inc.

In 1979, the Tokyo Electric Power Company, Inc. decided to introduce a
phosphoric acid type fuel cell test plant from United Technologies
Corporation for the purpose of demonstrating the performance of a fuel
cell plant on our electric power system. We started its construction at
our Goi thermal power station (total capacity 1760 MW, LNG fired power
plant) in August of 1980. The process and control test for the subsystem
of the plant excluding cell stack assembly was commenced in September 1981
and all tests were completed in October 1982. In November 1982, cell
stack assemblies were installed and we started overall operational testing
in April 1983 and achieved half load powerplant operation. During this
overall operational test, a local temperature increase on a reformer
tube was detected. As a result, we made reformer modification activities
in May through July, 1983 and resumed a ramp test of the plant in August
1983 which will be continued for about one year to verify the characteristics
of the plant in connection with our electric system.

55

ELECTRIC UTILITY PAFC TECHNOLOGY DEVELOPMENT PROGRESS

John M. Lee
United Technologies Corporation
Fuel Cell Operations
South Windsor, CT   06074

In 1978, United Technologies embarked on a major effort to reduce the cost of manufacturing and the cost of installation for electric utility fuel cell power plants relative to the 4.5-MW Demonstrator power plant. Improvements are being investigated for all the major subsystems - cell stack, fuel processor and power conditioner.

It was demonstrated analytically that increasing the operating pressure of the power plant allowed increasing rated power by a factor of more than two without increasing the size of many of the Demonstrator components. Concurrently an increase in cell size reduced the number of individual cells and the total parts count.

The power section changes are being verified as part of a DOE/NASA program. A stack of thirty 10 square foot cells has been constructed. Figure 1 shows the cell stack being installed on the pressure vessel base.

FIGURE 1   THIRTY - 10 SQUARE FOOT CELLS (50 kW)

An EPRI sponsored program has demonstrated 1000 hours of successful operation on a new full size reformer tube. This tube is larger than that used in the 4.5-MW Demonstrator and operates at a higher pressure. Figure 2 shows the reformer tube test facility.

FIGURE 2   SINGLE FULL SCALE REFORMER TUBE
TEST FACILITY (200 kW)

Improvements in inverter technology are being sought to increase capacity at lower cost. Programs sponsored by DOE and EPRI are investigating larger, higher voltage rated thyristors and an improved commutation circuit. Figure 3 shows a development switching pole which incorporates the advanced thyristors. A more advanced pole and a scale model system to test the advanced logic are under construction.

FIGURE 3   INVERTER DEVELOPMENT SWITCHING
POLE (1.2 MW)

WESTINGHOUSE FUEL CELL POWER PLANT DESIGN

Donald Newby
Westinghouse Electric Corporation
Advanced Energy Systems Division
P. O. Box 10864
Pittsburgh, PA   15236

INTRODUCTION

Westinghouse Electric Corporation is committed to the development of air cooled phosphoric acid fuel cells for both all electric and cogeneration applications. To this end, Westinghouse along with DOE/NASA, EPRI, and ESEERCO are providing funding support for the design of two 7.5 MWe DC power plants scheduled for initial operation in 1987 and 1988. The effort is divided into a technology program which is concerned with the fuel cell development and a plant design program. This paper will discuss the plant design program with particular emphasis on long term commercial application.

PLANT DESIGN OBJECTIVES

The objective of the prototype plant program is to develop prototypes which are as close as possible to the final commercial product and to provide features which will allow easy adaptation to future customer requirements.

The principle advantages offered by fuel cells are short construction time, cost-predictability, efficiency, reliability, and ease of siting. These advantages can only be achieved with a factory produced modular design which is pretested to the maximum extent possible before shipment to the field. As a result of these features, our studies foresee a total market by the year 2000 between 700 and 1200 MW/year providing cost goals of less than $1000/kW and heat rates of less than 8000 Btu/kW are met. The bulk of this early market is expected to be plants sized between 5 and 50 MW with cogeneration applications being an important segment. A 7.5 MW sized prototype plant was chosen since above 7.5 MW the heat rate gain is small and this size allows a modular approach for larger plants while keeping all components shippable by truck.

In addition to the size considerations, the makeup of potential customers, and their specific requirements must also be satisfied without major redesign. It is expected that these future customers will fall into the following general categories:

- Utilities - All Electric
- Utilities - Cogeneration
- Industry - Cogeneration
- Industry - H_2 Fueled

These customers may be located in diverse areas of the country, therefore, the potential for high seismic activity, freezing, and water shortage is being factored into the design.

The design of the prototype power plants, as presently conceived is for "all electric" or "cogeneration" applications in a warm climate. Each major operating segment of the plant has been confined to independent "islands" which allows relatively easy adaptation to various requirements.

For instance, this plant can be adapted for colder climates since the design allows for enclosing portions of the fuel processor and the fuel cell island. The "island" approach to the layout also allows adaptation for industrial sites which have hydrogen available from other sources by simply removing the fuel storage and fuel processor islands without affecting the remainder of the plant.

Plants having capacity requirements of more than 7.5 MW will require duplicates of the fuel cell island and the fuel processor island. The island containing the balance of plant systems will be modified to increase their capability to service the entire plant. This can be done without affecting the layout of the other islands.

A FUEL MOTIVATED APPROACH TO
FUEL CELL APPLICATION

J. W. Griswold and J. Wilborn
Southern California Edison
Rosemead, CA 91770

Abstract

Current emphasis on fuel cell power plant commercialization programs is based on the thermal and electrical efficiency of natural gas and naptha fuels. This paper places its main emphasis on the versatility of the fuel cell power plant which enables it to use non-conventional "waste fuels," focusing on gases produced by landfill and sewage treatment facilities.

Many studies and some demonstrations are being conducted for the conversion of industrial/agricultural by-products to usable fuels. Landfills and sewage treatment facilities produce off-gases that can be converted to pipeline quality gas or used on-site for heat, power, or cogeneration. Conventional generators capable of using these gases are, however, relatively inefficient and can present environmental problems when compared to fuel cell power plants.

The gases produced by landfill and sewage treatment facilities do not meet fuel specifications set by the fuel cell manufacturers. There are many components of these gases that have unknown effects or are harmful to the fuel cell operation. Existing methods and commercially available equipment can convert these gases to fuel cell quality; however, there are questions about sizing and economics of these gas purification systems that must be investigated.

Although landfill and sewage treatment facilities have been identified as good potential fuel sources for fuel cells, there are many other types of industrial/agricultural businesses that also have potential of producing usable waste fuels. It is likely that usable waste fuels exist in most utility territories. The identification and resource size estimation of these non-traditional fuel resources can enhance the commercialization of all sizes of fuel cell power plants.

A development program for fuel cell power plant commercialization needs to include gas clean-up system development and fuel source identification is discussed. An ideal program to start such development is the Gas Research Institute/U.S. Department of Energy 40-kW fuel cell power plant demonstration. The small size of this fuel cell power plant limits the expense of the gas clean-up system development yet will yield information that will be directly applicable to other sizes of fuel cell power plants.

Introduction

The current emphases of the current phosphoric acid fuel cell power plant commercialization programs are the thermal and electricity power generation, siteability, and overall efficiency compared to conventional power plants. All this is based upon conventional fossil fuels; the 40-kW program uses natural gas and the multi-megawatt programs assumes natural gas and naptha, with some effort directed towards coal-derived fuels.

The approach discussed here puts more emphasis on fuel utilization, rather than the normally noted efficient power generation, and looks to fuel cell applications that use "non-conventional" fuels that are now being wasted, flared, or used in some less than optimal application. Of particular interest is landfill gas and sewage treatment gas.

Also discussed is a possible program that incorporates 40-kW size units to develop and demonstrate fuel versatility and appropriate gas clean-up systems. Such a program would lead to both conventionally- and nonconventionally-fueled applications for 40-kW type power plants as well as multi-megawatt power plants. Fuel versatility that includes this type of nonconventional fuels would only broaden the commercial acceptance of fuel cell power plants.

Nonconventional Fuels

Much effort has been directed towards converting various industrial/agricultural by-products to usable fuels. Two existing industries that currently produce and dispose of gaseous, methane-rich by-products that appear very promising for fuel cell power plant use are landfills and waste water treatment or sewage treatment facilities. Various methods have been used by both types of facilities to make use of a portion of the by-product gases produced (1). These methods range from producing pipeline quality gas for resale, to the on-site use for heat, power, or cogeneration. Studies have shown that it is more economical to use this by-product on-site than to produce pipeline quality gas (2). The conventional generation equipment typically used on these sites, however, may leave the operator with unsolved, or expensive, noise and emission abatement problems.

The fuel cell seems to be an ideal application for this fuel source. Not only would power and heat be generated efficiently, but any noise or emission problems would be eliminated; however, these problems are traded for gas clean-up needs. Table 1 shows some emission comparisons.

62

Gas Clean-up

The two nonconventional fuel sources mentioned, do not provide gases that meet current fuel cell specifications. In fact, some sources do not produce a gas with a consistent composition.

Generally, landfill gases contain about 48 percent methane and 35-42 percent carbon dioxide, while digester gases have 50-65 percent methane and 34-37 percent carbon dioxide. Both gases have an approximate heating value of 500 Btu/SCF. The compounds that must be removed or reduced include: carbon dioxide, heavy hydrocarbons and other trace elements. Heavy metals in digester gases must also be removed. During the process of pumping out landfill gases, air is entrained and must be removed to obtain fuel cell quality gas.

CO_2 is another component that requires removal as the fuel cell can accept no more than 3 percent CO_2. Landfill and digester gases contain about 35 percent CO_2. In itself, CO_2 is not a poison, but is undesirable due to the volume it occupies.

Table 2 shows an average fuel specification, and Table 3 shows constituents of landfill and digester gases.

Quantifying the Fuel Source

The nonconventional fuel sources described, and other potential fuel sources not mentioned, probably exist in most utility service territories. With the range of fuel cell sizes being commercialized (40-kW to 11-MW modules), almost any size source of fuel is of interest. It seems likely the gas producers (intentional or otherwise) will welcome fuel cell installations, both from a revenue and abatement standpoint.

Although landfills and sewage treatment plants are used for discussion here, the search for nonconventional fuels need not be limited to these processes and installations. Many industrial and agricultural processes produce a gaseous by-product or waste stream and are potential sources of nonconventional fuels (3).

Identifying and exploring the nonconventional fuel sources available can only enhance the commercialization of all fuel cells. Showing that fuel cells can be used to extract useful energy from otherwise nonutilized gas streams will be a positive force in the overall commercialization effort. This fuel-oriented approach may identify a new application market outside the traditional energy industries.

A Development Program

The necessary development program must include gas clean-up system development as an integral facet. Although many commercial systems exist, it is not obvious that they can be designed in a small size, while able to handle varying input streams and be nonpolluting.

The 40-kW fuel cell, now in the midst of a commercialization program (4), is the ideal size for such a development program. The size limits the expense of the gas cleaning equipment, but process data and know-how that will be obtained will be applicable to all presently contemplated sizes of phosphoric acid fuel cell power plants. In addition, the 40-kW size lends itself to direct application in utilizing smaller-sized gas stre----.

The program envisioned will have three main parts: 1) Gas clean-up system development; 2) Fuel cell power plant commercialization; and 3) Fuel source identification.

The gas clean-up system development can be started and, in fact, implemented before the power plant is installed. Such a system must demonstrate its ability to produce a useable output steam before power plant installation is contemplated. After installation, there may be some potential for exploring the real tolerance levels of fuel cells for gas clean-up systems. This is, however, a risk-filled area and needs further definition.

The fuel cell power plant commercialization programs now underway are the backbone of this or any other fuel cell utilization activity. These current programs must not be interfered with. Therefore, the first prototype demonstrations have (in the 40-KW case) and should (in the multi-megawatt case) be completed with the design fuel of natural gas. To begin with a non-conventional fuel in conjunction with a potentially developmental clean-up system would be an improper complication. Commercial installations with non-conventional fuels would, however, closely follow the first prototype demonstrations.

The fuel source identification is an activity that can be completed independently of power plant commercialization. The potential fuel sources need to be identified early, however, in order to define gas clean-up requirements. Figure 1 shows a simplified program Flow Chart.

When all three aspects of such a program are complete, the utility will be in a position to utilize fuel cell power generation installations of all sizes fueled by conventional fuels and fuels not now used for power generation.

Conclusions

Current fuel cell commercialization activities are based on conventional fuels--natural gas and naptha. Commercialization efforts would be enhanced if other applications for fuel cell power plants could be identified and demonstrated. Nonconventional fuel sources offer a potential for another attractive application.

These fuel sources need to be identified and quantified. In addition, applicable gas clean-up systems need to be developed and demonstrated. The current 40-kW fuel cell field demonstration program is the ideal vehicle for developing gas clean-up systems and demonstrating the viability of nonconventional fuel source applications.

Such applications would be an enhancement of current fuel cell commercialization efforts. One deterrent to wide-spread utility acceptance of fuel cells may be a reluctance to embrace another conventional fossil-fueled generation device. By showing that non-traditional fuels are useable and available, such concerns will be diluted.

References

1. S. C. James, C. W. Rhyne, "Methane Production, Recovery, and Utilization from Landfills," U.S. EPA.

    R. J. Neary, "Los Angeles County Combined Cycle Project," Solar Turbines Inc.

2. P. Pietrogrande, "A Preliminary Examination of Landfill Gas Treating Equipment and Consequent Landfill Gas Plant Levels in Southern California," KTI, 16 Dec. 1982.

3. J. Dobyns, and W. C. Racine, "By-Product Fuels for Power Generation," 25 Feb. 1983.

4. "40 kW Phosphoric Acid Fuel Cell Field Test," GRI, NASA, Nov. 1981.

TABLE 1 (3) (4)

EMMISION COMPARISONS (pounds/day)

Agency/Unit	Fuel	NO$_x$	SO$_x$	Partic-ulate	CO	Hydro-carbons
U.S. EPA		220	220	140	550	220
SCAQMD		100	150	150	550	75
40-kW Fuel Cell	SNG	3.84	0.0058	.0006	-0-	-0-
11-MW Fuel Cell	SNG	44.2	0.067	0.0067	-0-	-0-
500-kW Gas Turbine	SNG	100	150	0.3		
8-MW Gas Turbine	SNG	1116			76.8	96.0
	Diesel	1480.8		28.8	28.8	28.8
15-MW Comb Cycle	Digester Gas	2476.8	211.2	196.8	456.0	760.8
2-MW Reciprocating Gen.	Digester Gas	5311.2	187.2	160.8		

*Based on available data.

TABLE 2

Typical Fuel Cell Fuel Specifications*

COMPONENT	MAXIMUM ALLOWABLE VOLUME %
Methane	100.0
Ethane	10.0
Propane	5.0
Butanes	1.25
Pentanes, Hexanes C_6+	0.5
CO_2	3.0
O_2	2.5
N_2 (Continuous)	15.0
Total Sulfur	30 PPM_V
Thiophane Sulfur	10 PPM_V
NH_3	1 PPM_V
Chlorine	0.05 PPM_W

*United Technologies Corp.

40-KW Phosphoric Acid Fuel Cell

TABLE 3

Gas Composition Samples (Volume %)

Component	Natural Gas	Digester Gas	Landfill Gas
CH_4	>75	62	56
CO_2	<3	35	38
H_2O		1	
N_2	<15	0.83	3.0
O_2	<3000	0.17	1.0
H_2			0.3
NH_3	<10		
CL	<0.05	<10 $\mu g/m^3$	
Total Sulfur	<30		
C_2H_6	<10	0.002	26 PPM
C_3H_8	<5	<100 PPM_v	142 PPM
C_4H_{10}	<1.25	<100 PPM_v	104 PPM
C_5 and >	<0.5	<100 PPM_v	3.1-506 PPM
N_a		<80 $\mu g/m^3$	184-596 $\mu g/m^3$
K		<18 $\mu g/m^3$	2-36 $\mu g/m^3$
V		<40 $\mu g/m^3$	1.71-6.02 $\mu g/m^3$
Pb		<20 $\mu g/m^3$	1.5-23.8 $\mu g/m^3$
Fe		<10 $\mu g/m^3$	20-162 $\mu g/m^3$
Zn		<3 $\mu g/m^3$	147-480 $\mu g/m^3$
Ca		<10 $\mu g/m^3$	1650-4370 $\mu g/m^3$
Mg		<8 $\mu g/m^3$	152-428 $\mu g/m^3$
Cu		<4 $\mu g/m^3$	0.5-15.2 $\mu g/m^3$
Cd		<3 $\mu g/m^3$	2.05-5.45 $\mu g/m^3$
As		<80 $\mu g/m^3$	0.22-0.37 $\mu g/m^3$

FIGURE 1

Simplified Overall Program Flow Chart
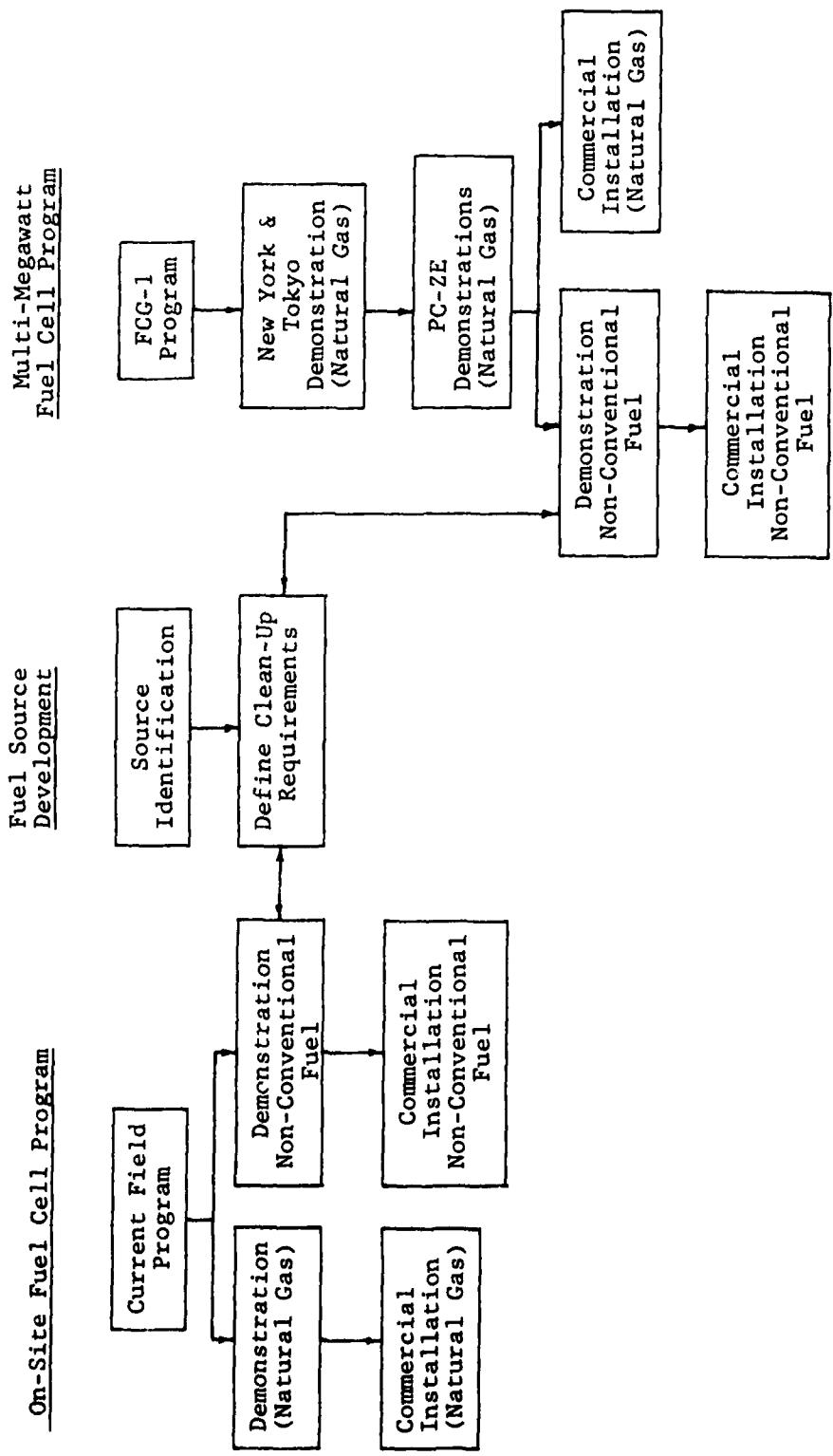
ASSESSMENT OF OPTIONS FOR
SMALL-SCALE LIGNITE FUELED
COGENERATION PLANTS

John R. Grisso
Ralph M. Parsons Co.
Pasadena, CA. 91124

Previous scoping studies sponsored by the Electric Power Research Institute (EPRI) indicate that small-scale power plants utilizing coal gasification and fuel cells show promise as a future source of power generation. The favorable results of these previous studies warranted further assessment of small-scale gasification fuel cell power plants.

The study reported herein was conducted by the Ralph M. Parsons Company under contract to EPRI for the purpose of providing a more detailed evaluation of such plants and to provide a comparison of fuel cell power plants with other alternate small-scale power generation technologies. The alternate technologies which were considered include a coal gasification/combustion turbine plant, an atmospheric fluidized bed boiler plant and a conventional direct-fired boiler plant. A summary of the plant configurations investigated is presented in Table 1.

The site selected for the plant is in an area outside of the city of Willmar, Minnesota. Willmar is located in the center of one of United Power Association's (UPA) 15-member distribution cooperative service area and UPA provided many of the site-specific design criteria used in the study. The site has been designated as a future industrial park where location of one or more industries having process steam requirements is contemplated. There is also an opportunity to utilize any available hot water from the power plant in a local district heating system in the city of Willmar.

The primary criteria for the plant were use of North Dakota lignite as fuel and cogeneration of electric power and approximately 100,000 lbs/hr of 175 psia process steam for export to the industrial park. For purposes of maintaining the comparisons of all plant configurations on an equivalent basis, a nominal lignite feed rate of 740 tons per day was used for all four configurations.

The results of the study are summarized in Table 2. Optimized conceptual designs, performance data and capital and operating costs were developed for each configuration. Using these data, the bus-bar power costs were developed. Revenues for process steam sales and/or district heating were used to off-set operating costs. Credits were also taken for by-products such as lignite fines and recovered sulfur where appropriate. The bus-bar power costs were calculated on a levelized basis over a 30-year book life, a capacity factor of 80% and are expressed in constant January 1983 dollars.

The differences in the bus-bar power costs indicated for the gasification/ fuel cell plant, the fluidized bed plant and the direct-fired boiler plant cannot be considered significant given the estimated $\pm$ 15 percent accuracy of the capital and operating cost estimates. It is significant,

however, that the fuel cell plant shows similar results to the direct-fired plants in terms of bus-bar power costs even though the fuel cell plant has a much higher capital cost. This is due to the much higher overall thermal efficiency of the fuel cell plant as compared with the other configurations (over 50 percent more net power output and a somewhat higher process steam output).

The results indicate that the gasification/combustion turbine plant is not competitive with the other options. A primary reason for this is the large amount of power required (9.9 MW) to compress the fuel gas to the required combustion turbine inlet pressure.

A detailed environmental assessment was prepared for each configuration based on the site-specific environmental requirements and needs of the Willmar site. Such requirements were incorporated into the designs for all configurations including application of Best Available Control Technology (BACT) to all emission sources within the facilities. Be-cause the site is classified as a Class II area under Prevention of Significant Deterioration (PSD) regulations, it was desirable to develop system designs which would be exempt from PSD application requirements thus avoiding the complicated and time-consuming PSD appli-cation process. Results indicate that both the gasification/fuel cell plant and the gasification/combustion turbine qualify for PSD exemption.

The fact that the results indicate bus-bar power costs for the gasifi-cation/fuel cell plant that are competitive with direct-fired boiler plants is encouraging with respect to the future of coal-gasification/ phosphoric acid fuel cell technology. This is because little improve-ment in terms of capital costs and plant performance can be expected in the direct-fired boiler plants since these configurations incorporate mature technologies. This is not true of the gasification/fuel cell plant. Further development of such plants should result in significant reductions in capital costs and significant increases in overall plant efficiency. Therefore, such plants appear to be a viable alternative for small-scale generation using solid fuels.

Table 1

SUMMARY OF PLANT CONFIGURATIONS INVESTIGATED

Configuration Designation	I	II	III	IV
Plant Configuration	Lignite Gasification Fuel Cell	Lignite Gasification Combustion Turbine	Fluidized Bed Boiler	Direct-Fired Boiler
Fuel Preparation	Gasification/Water-Shift	Gasification	None	Pulverizing
Sulfur Removal Process	Stretford	Stretford	Fluidized Bed Boiler	Scrubber
Power Generation Cycle	Phosphoric Acid Fuel Cell/Combined Cycle	Combined Cycle	Rankine Cycle	Rankine Cycle
Main Power Generation	Fuel Cells	Combustion Turbine	Steam Turbine	Steam Turbine
Other Power Generation	Turbo-Expander, Steam Turbine	Steam Turbine	None	None

72

TABLE 2
SUMMARY OF RESULTS

	Lignite Gasification/ Fuel Cell Plant	Lignite Gasification/ Combustion Turbine Plant	Fluidized Bed Boiler Plant	Direct-Fired Boiler Plant
Gross Plant Power (MW)	50.50	32.22	23.50	24.29
Net Plant Output (MW)	32.48	20.12	20.59	21.18
Net Export Steam (lbs/hr)	106,950	100,420	100,000	100,000
Overall Plant Efficiency (%)	56.1	44.1	43.1	43.6
Total Installed Cost ($000)	111,431	90,515	73,658	69,313
Annual Expenses ($000/yr):				
Levelized Carrying Charge	7,912	6,427	5,230	4,921
Operation & Maintenance Cost	6,487	4,244	4,208	3,688
Fuel Cost	5,633	5,633	5,163	5,163
Total Expenses	20,032	16,304	14,601	13,772
Credits for Process Steam and Other Byproducts ($000/yr)	4,578	4,864	3,917	3,917
Net Power Cost ($000/yr)	15,454	11,440	10,684	9,855
Bus-Bar Power Cost ($/kWh)	0.068	0.081	0.074	0.066

Notes:
(1) All values in $ 1983.
(2) 90% capacity factor assumed.
(3) Levelized carrying charge and bus-bar power costs are calculated in accordance with EPRI Technical Assessment Guide (TAG) procedures for constant dollars (no inflation) and 30-year plant life.

RMP

73

MONOLITHIC FUEL CELLS

D. C. Fee, R. K. Steunenberg, T. D. Claar,
R. B. Poeppel, and J. P. Ackerman
Argonne National Laboratory
Argonne, Illinois 60439

A new fuel cell technology is being developed at Argonne National Laboratory. This new design concept, called the monolithic fuel cell, has roughly 100 times the power density of conventional fuel cells. The design employs the thin ceramic layer components of existing solid oxide fuel cells in a strong, lightweight honeycomb structure of small cells, and so achieves unequaled power per unit mass or volume. The monolithic fuel cell will convert hydrocarbon fuel to dc power at 50% efficiency, and thus attains considerably higher energy densities than other technologies that use non-exotic fuels.

In the monolithic concept, fuel and air are combined electrochemically in a ceramic cell at an operating temperature of 1100 to 1300 K. Cell components are fabricated as one piece much like a block of corrugated paperboard. Fuel and oxidant are conducted through alternating passages in the structure, as shown in Figure 1. These passages are formed from thin (25 to 100 micrometer) layers of the active cell components: the anode, cathode, electrolyte, and an "interconnection" material which serves to connect cells in electrical series (bipolar plate). The corrugations also form the gas seal at the edges of the structure. Advantage is taken of the ability to fabricate the solid electrolyte and other solid cell components into unique shapes which cannot be achieved in liquid electrolyte systems. In liquid electrolyte systems, much of the mass and volume goes into building the inert container for the liquid. Eliminating this unnecessary material gives the monolithic fuel cell a significant advantage in performance.

The high power density of the monolithic fuel cell results from the small cell size. Cells 1 to 2 mm in diameter or smaller are achievable when the inert container for electrolyte and the inert support for the thin active layers are eliminated. The small cell size increases the active surface area per unit volume of the cell. For example, a monolithic cell structure with approximately 1 mm diameter gas flow channels has an active surface to cell volume ratio of 10 cm^2/cm^3 compared to 1 to 2 cm^2/cm^3 for conventional fuel cells (PAFC, MCFC, SOFC). This reduces the volume of the fuel cell by a factor of five or more; larger reductions in volume are achieved by cell sizes even smaller than 1 mm. However, the resistance to gas flow also increases as the cell size is reduced. Gas flow resistance depends somewhat on the overall manifolding and generator design, which have yet to be optimized for a monolithic fuel cell system. Nevertheless, gas flow channels of 1 to 2 mm diameter and smaller appear feasible, based on operating experience in other systems.

More importantly, the small cell size in the monolithic
design reduces the voltage drop due to internal electrical
resistance. This is an important consideration, because
internal resistance is the principal dissipative loss for the
ceramic materials and temperatures of interest. Decreasing
the cell size decreases the current path length, because
current is carried in-plane by the electrodes in the mono-
lithic design. As shown in Figure 2, electrons (coming from
the adjoining cell in electrical series) flow through the
plane of the interconnection, then part way around the
circumference of the cell in the plane of the air electrode.
At the air electrode/electrolyte interface, the electrons are
consumed in the formation of oxide ions. The oxide ions are
transported through the plane of the electrolyte. At the
fuel electrode/electrolyte interface, the oxide ions react
with hydrogen (from reformed hydrocarbons) to form water.
The released electrons flow part way around the circumference
of the cell in the plane of the fuel electrode, then through
the plane of the interconnection into the next cell in
electrical series. The small cell size decreases the current
path length in the electrodes and reduces the voltage drop
due to internal resistance.

The high current density of the monolithic fuel cell
results from the small cell size and ensuing low internal
resistance. As a consequence of the low internal cell
resistance and the high driving force (Nernst potential) at
the fuel inlet, the current density is high at the fuel inlet
(and low at the fuel outlet) end of the fuel channel, as
shown in Figure 3. The low current density at the fuel
outlet is desirable, because overall cell performance is
determined by the voltage drop due to internal resistance at
the cell outlet. (Voltage losses arising from resistance to
gas phase diffusion are negligilble due to the thin elec-
trodes.) Small resistance polarization losses (1 to 5 mV) at
the fuel outlet mean that the fuel electrode, as an equi-
potential surface, approaches the maximum theoretical voltage
(Nernst potential) at the fuel outlet as set by thermodynamic
considerations. The optimum cell performance is obtained
when the average current density is increased to the point
where resistance polarization losses at the fuel outlet just
become significant, as shown in Figure 3. As a result, the
cell nearly always operates within a percent or so of the
maximum efficiency, even at high power output.

Monolithic fuel cells have high power densities as a
result of the high active surface area, high current density,
and low weight. The low weight results chiefly from the
elimination of inert materials to contain the electrolyte or
to support the thin active layers. In the monolithic design,
the thin ceramic layers are self-supporting over the small
distances involved. An additional weight reduction comes
about from thin electrodes, which are achievable due to the
short current paths. Again, there is a benefit of the
reduced cell size. The increase in power density accruing

from the small cell size is the major incentive for developing the monolithic fuel cell.

The principal challenge for the development of the monolithic fuel cell is the fabrication of the unique structures. The fabrication processes presently under evaluation include tape casting, slip casting, and extrusion. Studies aimed at defining the requisite processing/structure/ property relationships have been initiated with support from the Department of Energy and the Defense Advanced Research Projects Agency.
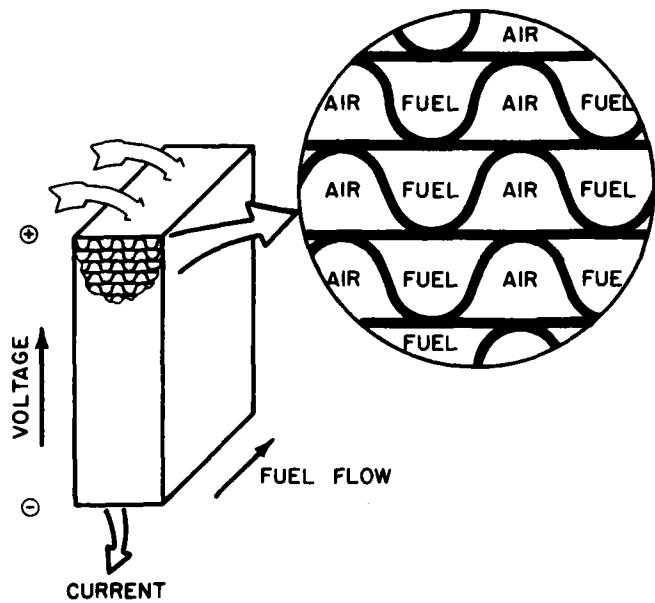
FIGURE 1

MONOLITHIC FUEL CELL

MONOLITHIC FUEL CELL
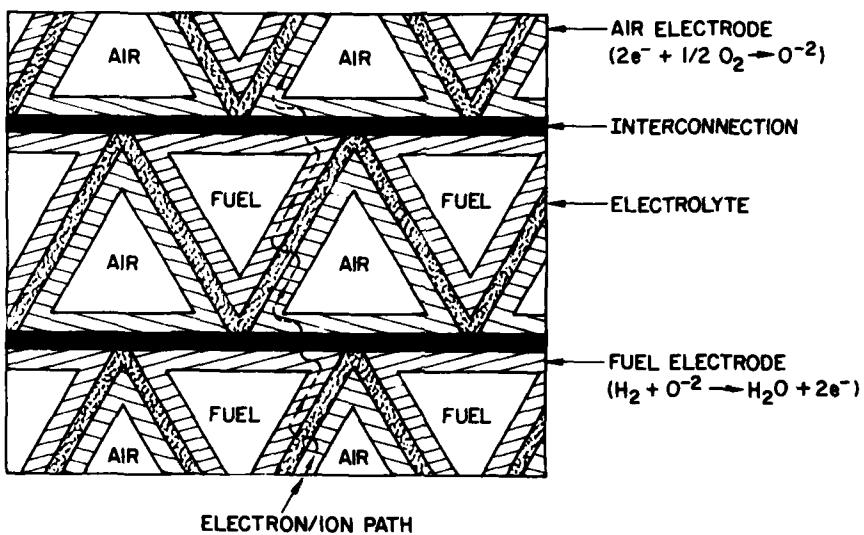
FIGURE 2

CURRENT FLOW PATH IN MONOLITHIC FUEL CELL

MONOLITHIC FUEL CELL
AXIAL CURRENT PROFILE
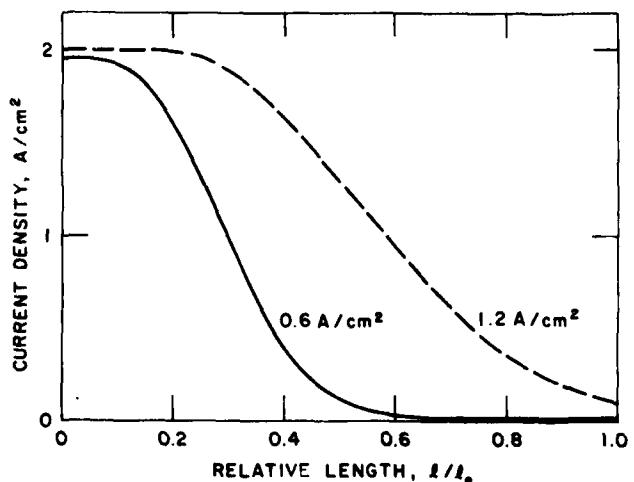
FIGURE 3

AXIAL CURRENT DISTRIBUTION ALONG FUEL CHANNEL FOR AVERAGE
CURRENT DENSITIES OF 0.6 and 1.2 A/cm^2. FUEL ENTERS AT
RELATIVE LENGTH 0 AND EXITS AT RELATIVE LENGTH 1.0.

ADVANCING FROM SINGLE CELL TECHNOLOGY
TO GENERATOR ENGINEERING (A SOFC STATUS REPORT)

Arnold O. Isenberg
Westinghouse Electric Co., R&D Center
1310 Beulah Rd., Pittsburgh, PA   15235

An advanced concept of solid oxide electrolyte fuel cell (SOFC) was disclosed recently.[1] This concept employs a tubular cell geometry, where individual cells are stacked together in a cubic dense pack, for achieving electrical cell-to-cell inter-connection. The cell geometry evolved from considerations for a practical generator design, where the high temperature of operation poses limits on structures and materials, yet, offers unique opportunities in design and process control.

Before detailed generator design and engineering can commence, however, cell performance and cell manufacturing techniques must have reached a level of maturity that minimizes the need to turn back to related basic development to obtain previously missed information. Often, extrapolation of single cell performance to module characteristics leads to over-optimistic assumptions, due to significant differences in reactant flow, reactant utilization, current and temperature distribution and other process control parameters, as pressure drop in reactant manifolds. A major structural consideration, the sealing of anode and cathode compartments, which is readily achieved in single cell test rigs, requires frequent re-evaluation when progressing from single cell tests to module tests.

All sealing schemes for SOFC-generators that had been proposed in the past were considered either too costly, unreliable in operation,or practically unworkable. The high temperature of operation for SOFCs(1000°C) offers here a unique opportunity, namely, that all fuel compositions, when combined with air, burn chemically to completion and, spontaneously, as long as excess oxygen is available. The basic SOFC generator design shown in figure 1 makes use of this opportunity.

Fuel gas, consisting of hydrogen and carbon monoxide mixtures (any ratio), surrounds the cell tubes and flows from one reactor end through the bundle of cell tubes in an axial flow path. The cell tubes are closed end at the region of fuel entry. Fuel is electrochemically consumed along the tube active cell length and combustion products and residual fuel flow through a porous ceramic fiber diffusion barrier. Air enters the cell interior by means of an alumina (or other) tube, reverses flow direction at the closed end of the cell tube and oxygen is taken up electrochemically while passing downstream. The oxygen depleted air combines, then, with the fuel combustion products. An excessive amount of air accomplishes cell cooling while combustion of residual fuel, in combination with the sensible heat of effluent gases, preheats the air before it comes in contact with the actual cell structure. The basic SOFC generator scheme, therefore, integrates a high-temperature heat exchanger and cell bundle, eliminating the need for any gas tight seals. The power take-off is accomplished in the reducing environment of the fuel compartment with metallic conductors.

Figure 2, depicts, schematically, a test envelope that serves
well in testing aspects of cell operation in a generator envir-
onment, as described above. Current flow, fuel-and air-flow,
as well as the "seal-less" concept of combining spent fuel and
spent air are subject of each cell testing procedure. To date,
no serious obstacle has been encountered in the cell design and
in operational parameters of cells as they relate to the basic
SOFC generator design.

Recently obtained performance characteristics of cells demon-
strate considerable improvement in cell performance, as shown
in figure 3. This performance level of cells is very close to
that calculated from cell component properties. Figure 3
shows a VI-curve for a prototype cell under constant fuel
utilization conditions, i.e., at all cell voltages, the fuel is
electrochemically oxidized to the level of 80%. Fuel flow to
the cell was varied to achieve different current density levels.
Such cell characteristics are the only meaningful guideline to
extrapo. te to fuel cell plant characteristics, plant-cost,
and plant-efficiency.

While air is considered to be the only practical oxidizer,
oxygen is used in cells to demonstrate the maximum potential
of the air electrode. Figure 3 shows, also, the cell behavior
when using pure oxygen. It becomes clear from the comparison
of air versus oxygen that further improvement of cell perfor-
mance can be obtained by minimizing the "barrier effect" of
the porous support tube-air electrode combination. This can
be accomplished by reducing tube and electrode thickness and
increasing porosity (a task that will continue even when SOFCs
have reached the market place).

Figure 3 also shows the linearity of the ohmic cell overvoltage
with varying current. This voltage drop agrees closely with
calculations from cell component bulk resistivities and thick-
nesses. Further improvement of cells, therefore, can mainly be
achieved by reducing electrode resistance. Air electrode over-
voltage can be determined from the comparison of cell perfor-
mance under oxygen and air as oxidant. Adding up air electrode
concentration overvoltage and internal resistance drop, one
comes to the conclusion that the thin fuel electrode exhibits
very little observable concentration overvoltage, therefore,
leaving no room for further cell performance improvement
through fuel electrode optimization.

Considerable progress in cell performance stability has been
made also. Cell performance is essentially flat over hundreds
of hours in recent cells and stable internal ohmic resistance
has been achieved from the onset of cell testing with cell
components that are considered to be practical candidates
for commercial generators.

The rapid progress in SOFC development has led this technology
to a level of maturity in cell performance, performance sta-
bility, reproducibility and processing techniques that warrants
the initiation of detailed design, engineering and construc-
tion of generator hardware.

Acknowledgement

Journal Articles

1. A. O. Isenberg, "Recent Advancements in Solid Electrolyte Fuel Cell Technology," National Fuel Cell Seminar Abstracts, November 14-18, 1982, pp. 154-156.
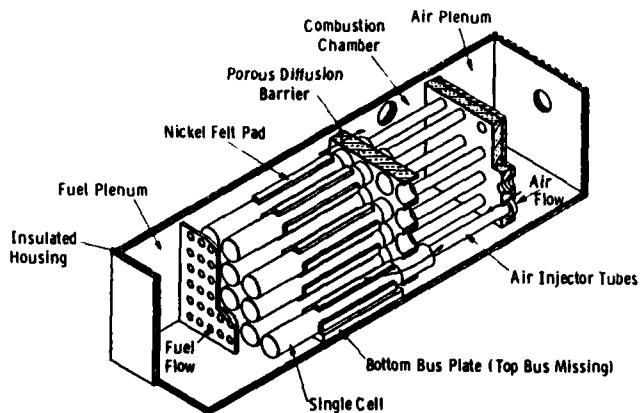
Fig. 1—Schematic design of SOFC generator
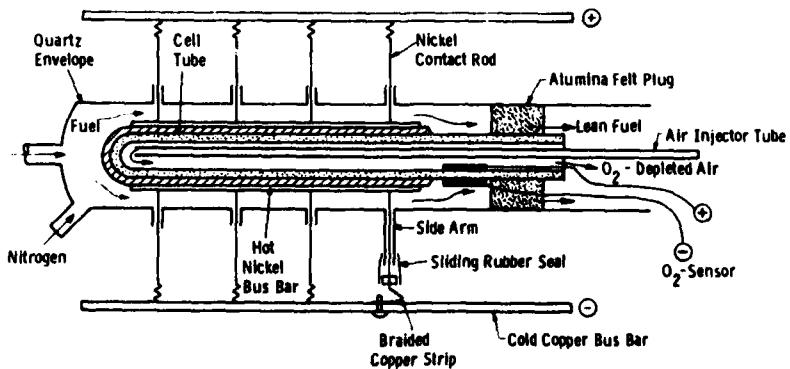
Fig. 2—Single SOFC test envelope with seals, contacts and reactant flow
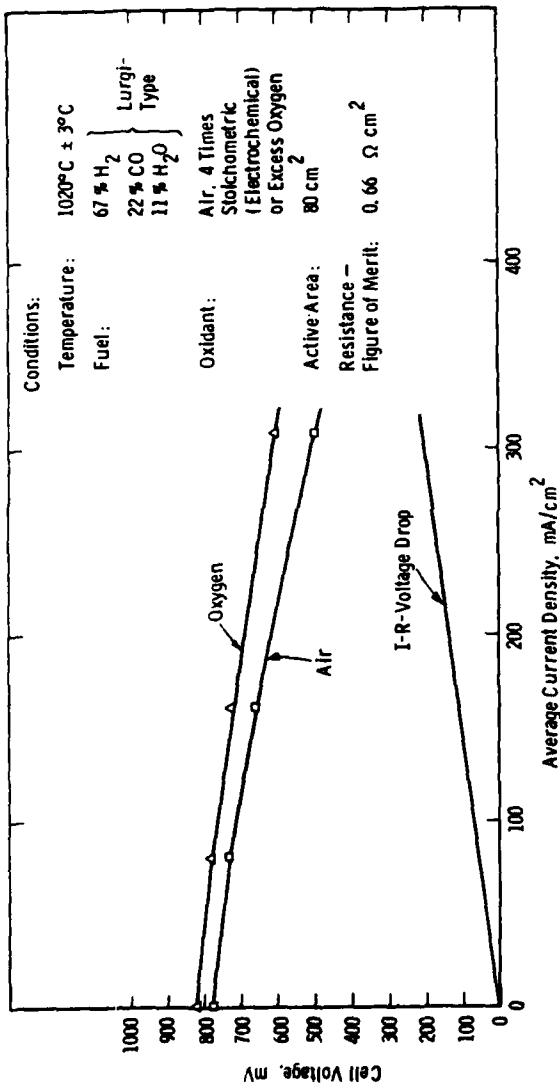
Fig. 3—V-I characteristics of state-of-the-art solid oxide fuel cells (constant fuel utilization 80 %)

Conditions:

Temperature: 1020°C ± 3°C

Fuel: 67 % H_2 }
22 % CO } Lurgi-Type
11 % H_2O }

Oxidant: Air, 4 Times Stoichometric (Electrochemical) or Excess Oxygen

Active Area: 80 cm^2

Resistance – Figure of Merit: 0. 66 Ω cm^2

COMPUTER-BASED FUEL CELL ANALYTICAL
TOOLS: DESCRIPTION AND AVAILABILITY

by

C.M. Zeh, F.D. Gmeindl, and R.A. Bajura
U.S. Department of Energy
Morgantown Energy Technology Center
Morgantown, WV 26505

The Morgantown Energy Technology Center (METC) is the U.S.
Department of Energy lead center for fuel cell technology and
has the responsibility for advancing the development of this
potentially attractive option for electrical power generation.
In support of this advancing technology, METC is developing
the capability to simulate the overall performance of phos-
phoric acid, molten carbonate, and solid oxide fuel cell sys-
tems using computer models. These models will be useful for
evaluating competing fuel cell systems on a common basis and
for identifying the technological issues with the greatest im-
pact on system cost effectiveness.

In recent years, a number of organizations have been involved
in developing computer models which are capable of predicting
various aspects of the performance, economics, and environ-
mental intrusion of both individual cells and complete fuel
cell power generation systems. Cell performance models have
been developed which predict operating characteristics such as
heat and mass transfer, fuel utilization, current density, and
the effect of contaminates on cell operation. These models
are either steady-state or transient with the transient models
being used to simulate the dynamic response of the system
during load- following maneuvers. Some of the performance
models are theoretical in approach and are based on fundamental
principles of thermodynamics and mass transfer. Because theo-
retical models simulate the operating mechanisms of fuel cells,
these models provide analytical insight into the optimization
of overall system operation. Other empirical performance mod-
els use correlations derived from experimental data. Comple-
menting the performance models, other codes have been developed
to provide an economic analysis of fuel cell systems and to
identify the end use application of these systems under a
variety of marketing condition scenarios.

This paper describes the results of a review which was made to
identify existing fuel cell models and to determine the avail-
ability and the applicability of these computer codes for fuel
cell simulation at METC. The models are categorized by the
type of fuel cell system to which they apply. The algorithms
and the calculational procedures used in coding the model are
discussed. Models which are in the public domain are treated
in more detail than proprietary models. The major input and
output parameters of the model are identified together with
the operating conditions and the cell stack size for which the
model is applicable. For performance models, an estimate is
given of the extent to which the model has been validated with
experimental data and the results of this validation exercise.
The computer operating characteristics which are given for all
models include: the system and language which was used in

developing the model, average CPU time to execute the model, and the core space requirements. An indication is made of the amount of internal documentation in the code and the availability of user manuals is noted.

COMPUTER MODEL OF UTC 11-MW
FUEL CELL POWER PLANT

R. L. Rentz, A. U. Hira, A. J. Parker, J. S. Moore
Mueller Associates, Inc.
Baltimore, MD   21227

A fuel cell computer model is being developed under the sponsorship of the U.S. Department of Energy by Mueller Associates, Inc. The computer code evaluates the system technical performance and related economics of the United Technologies Corporation's FCG-1, 11 MW, power plant conceptual design for various operating conditions. Operation of the computer program is designed in a "user friendly" mode so that technically-oriented individuals unfamiliar with the details of fuel cell technology can successfully operate the code. The computer code is designed for use on a TRS-80 Model II microcomputer, but can be adapted to and accessed through compatible machines. The code is designed to be applications oriented and is not a fuel cell power plant design tool.

The computer model is designed and constructed using a systems approach. This approach resulted in the logical separation of the analytical effort into five major segments. These five segments represent the four major power plant subsystems (the fuel processing, cell stacks, air pressurizing, and thermal management sub-systems) and a complementary economics routine. The analytic routines are based upon conventional thermodynamics supported by empirically-based parametric relationships.

Because the model is intended to explore technical issues associated with fuel cell technology, the operating conditions in the fuel cell stacks are a primary driving force for the model. Therefore, basic inputs to the program include the desired operating conditions for the fuel cell stacks. On the basis of these conditions, material and energy balances are determined throughout the power plant system. The cell stack model resulted from an intensive review and analysis of cell stack research data and utilizes empirically based parametric relationships to calculate voltage/current outputs. Specifically, the cell stack code can evaluate the effects of variations in pressure and temperature; hydrogen, oxygen, carbon monoxide (and other contaminants) concentrations; hydrogen and oxygen utilization rates; and stack aging on system performance and economics.

The economics routine will allow for the simultaneous determination of system economics for each run of the program. The economics routine is modeled utilizing the Electric Power Research Institute's recommended guidelines. (1)

The presentation will define the current status of the Mueller Associates modeling efforts.

References

1. "TAG Technical Assessment Guide," Electric Power Research Institute Special Report, P-2410-SR, May 1982.

NATIONAL FUEL CELL SEMINAR (1983) PROGRAM AND ABSTRACTS
HELD AT ORLANDO FLORIDA ON 13-16 NOVEMBER 1983(U)
DEPARTMENT OF DEFENSE WASHINGTON DC 1983

UNCLASSIFIED

F/G 10/2 NL

END
DATE
FILMED
10-84

DTI
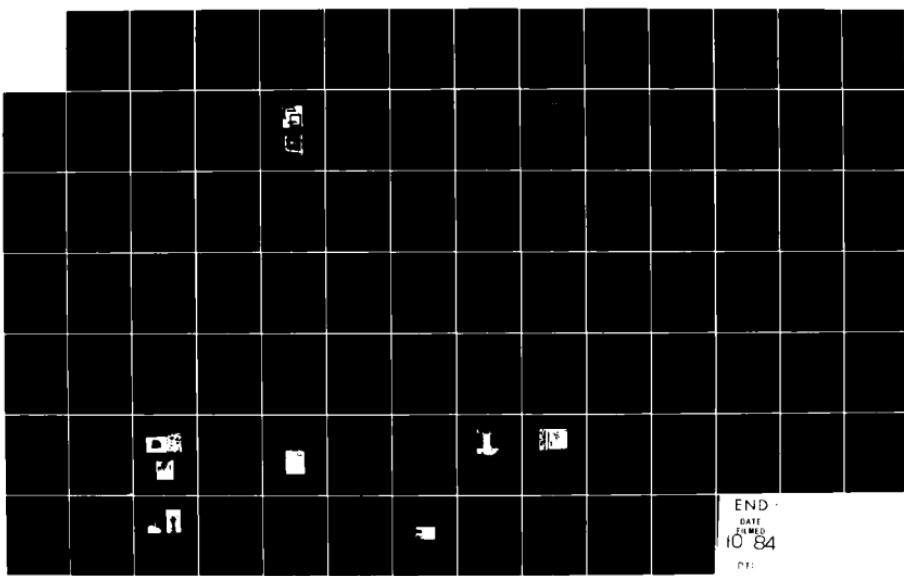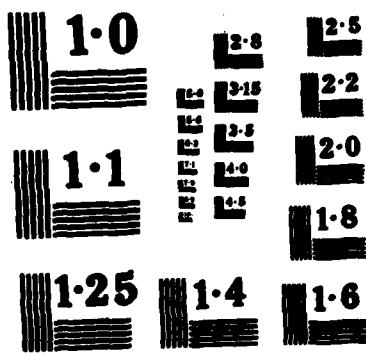
PSI: MECHANISTIC FUEL CELL MODELING

G. Wilemski and A. Gelb
Physical Sciences Inc.
Research Park, P. O. Box 3100
Andover, MA 01810

Over the past five years under DOE and EPRI support, Physical Sciences Inc. (PSI) has developed highly sophisticated models capable of predicting fuel cell and electrode performance over a wide range of operating conditions. The nature of the PSI fuel cell modeling work, the kinds of results that can be calculated and their value to the fuel cell program are discussed below.

Two levels of fuel cell performance modeling are performed at PSI. The first concerns the prediction of overall cell performance and performance decay[1,2], i.e., the calculation of current-voltage curves and their decay rates for various cell operating conditions. The second involves the determination of individual porous electrode performance[3-6], i.e., how the electrode overpotential is affected by pore structure, gas composition, degree of electrolyte fill, etc. Both levels are mechanistic, as opposed to empirical, using fundamental mathematical descriptions of the relevant physical and chemical phenomena, and provide quantitative predictive capability.

Porous Electrode Models

Individual porous electrode models form the basis for calculating cell performance. These models are used to determine the current density in regions of the cell small enough such that the local operating conditions are approximately uniform. The models in current use[3-6] are based on earlier work on the thin film model[7,8] and the flooded agglomerate model[9], and they consist of mechanistic treatments of the different microscopic phenomena occurring in the electrode. In accounting for electrode performance over a broad range of operating pressures and gas compositions, this type of approach affords a measure of versatility that is difficult to achieve with empirical models. This statement is supported by our model's ability to account for performance of isothermal 94 cm^2 cells at IGT[10] for several different combinations of oxidant and fuel mixtures at different operating pressures and over a range of operating temperatures using the same set of values for the internal model parameters[1,2].

Overall Cell Performance Model

The theoretical prediction of large cell performance may advantageously be broken into three distinct tasks: use of porous electrode models to calculate local current densities and overpotentials in the cell; treatment of gas stream mass transfer effects in order to calculate local gas phase compositions; and the formulation of a comprehensive

85

heat transfer scheme in order to calculate local cell and gas temperatures.

The mathematical solution of these highly coupled problems is carried out numerically. Besides calculating average current density versus cell voltage, the PSI computer code also produces detailed spatial distributions of temperature, current density and reactant utilizations. The code was originally designed to treat cross-flow, co-flow and counter-flow geometries. Recently, under EPRI funding, the code's capabilities have been extended in two ways. Direct internal reforming of methane with finite rate kinetics can now be handled. The code's heat and mass transfer schemes have also been modified to treat a new flow geometry: U-flow. The U-flow geometry consists of two coupled cross-flow cells (or stacks). With both oxidant and fuel streams passing through the cells in series. Fresh oxidant enters the first cell while fresh fuel enters the second cell. Preliminary calculations indicate that U-flow results in slightly higher performance levels and more uniform temperature distributions than standard cross-flow cells.

Uses for Performance Model in Fuel Cell Program

The fuel cell and electrode performance models can be used advanteously in a number of ways to provide insight and information that might be too difficult, costly and/or time consuming to obtain experimentally.

First, the models enable an investigator to evaluate test cell-stack performance in-depth by varying fuel/oxidant compositions, utilizations, inlet temperatures, total pressure and flow configuration. Study of the detailed model calculations allows more precise conclusions to be drawn. It is possible to compare performance of different developers' cells on an equitable basis. The model can be used to distinguish "true" performance differences from "apparent" changes due to different operating conditions.

Also, the models can be used to: 1) establish performance goals to be met by improved cells and stacks and 2) search for changes of cell design and/or operation that show promise of giving the largest performance gains. Novel concepts such as direct internal methane reforming and new flow geometries can easily be evaluated for their effects on performance. Another use is to provide realistic performance levels for power plant systems analysis work.

An important use for these models is in the design of more efficient electrodes. The models allow one to evaluate performance changes due to variations in the structural design of components and in material properties. Variables that can be studied include the porosity and thickness

of electrodes, the conductivity of electrolyte and electrode material, and the degree of electrolyte filling of electrodes. The models have the capability to translate changes in electrode structure directly into perceivable consequences for the competing kinetic and transport processes within the electrode. In this way different electrode designs can be evaluated and those offering the "best" compromise among the competing processes can be selected. A related use is in assessing the causes of performance decay in time. The mechanistic formulation of the models permits incorporation of models for decay phenomena such as sulfur poisoning, electrolyte loss and electrode sintering.

Future Directions

Emphasis is presently being given to developing more realistic porous electrode models. These models form the basis for the calculation of overall cell performance and it is very important that they be as realistic and comprehensive as possible.

The current cathode model is based on the flooded agglomerate model and was developed under two previous DOE programs(5,6). This model depicts the electrode as an assemblage of spherical porous NiO grains partially filled by electrolyte. This is a realistic representation of the basic electrode structure. Our theoretical analysis of this model has resulted in an analytical expression for the current density-overpotential relation that accounts for electrode kinetics, liquid phase diffusion of reactants and ionic conductivity of electrolyte in the electrode. Not included in the model are effects due to: limited gas phase diffusion; reduced electronic conductivity of the electrode material; excess wetting by electrolyte; and smaller catalyst grains with non-uniform active surface. Because of these omissions the present cathode model requires extension to provide a more accurate measure of performance in the following situations: 1) at high current densities and/or at low reactant partial pressures where gas phase mass transport may become limited; 2) for electrodes that are too thick; 3) for electrodes that are too highly filled by electrolyte; 4) for electrodes using small catalyst grains in order to minimize liquid phase diffusion limitations.

The current anode model is a truncated thin film model in which the length of the film in the pore equals the pore diameter(3). This seems to be a reasonable model for the sparingly wetted Ni electrodes used several years ago. However, current anodes are made from a Ni-Cr alloy and the Cr oxidizes in situ to form a porous scale covering the NiCr substructure. This porous scale is readily wetted by the molten carbonate electrolyte. Thus the current anode structure is different from that underlying the model in use.

Even though this model appears adequate for calculating over-
all cell performance levels, a modified porous agglomerate
model is essential for use in detailed diagnostic or design
applications. Work along these lines is in progress.

The overall cell performance model is currently being
extended to include the effects of vertical concentration
gradients in gas distribution channels. These gradients pro-
duce additional gas phase diffusion overpotential losses.
These losses are expected to be more prevalent at higher cell
operating pressures due to higher local current densities at
higher cell utilizations and when dilute reactant mixtures
are used.

REFERENCES

1. Wolf, T. L. and Wilemski, G., "Molten Carbonate Fuel
   Cell Performance Model," J. Electrochem. Soc. 130, 48
   (1983).
2. Wilemski, G., Gelb, A., and Wolf, T. L., "Modeling of
   Performance and Electrolyte Loss in Large, Nonisothermal
   Molten Carbonate Fuel Cells," to appear in Proceedings
   of the Symposium on Molten Carbonate Fuel Technology
   (Electrochemical Society, Pennington, NJ, 1983).
3. Wilemski, G., "Simple Porous Electrode Models for Molten
   Carbonate Fuel Cells," J. Electrochem. Soc. 130, 117
   (1983).
4. Wilemski, G. and Gelb, A., "Some Implications of Porous
   Electrode Models for Cathode Reaction Mechanisms in Mol-
   ten Carbonate Fuel Cells," to appear in Proceedings of
   the Symposium on Molten Carbonate Fuel Technology (Elec-
   trochemical Society, Pennington, NJ, 1983).
5. Wilemski, G., Mitteldorf, J. and Simons, G., "Diagnostic
   Fuel Cell Model," PSI TR-317, May, 1982.
6. Wilemski, G., "Mathematical Modeling of Fuel Cell Elec-
   trodes," PSI TR-350, October 1982.
7. Srinivasan, S. and Hurwitz, H. D., Electrochimica Acta
   12, 495 (1967).
8. Wasan, D. T., Schmidt, T. and Baker, B. S., Chem. Eng.
   Prog. Symp. Ser. 63(77), 16 (1967).
9. Giner, J. and Hunter, C., J. Electrochem. Soc. 116, 1124
   (1969).
10. "Fuel Cell Research on Second-Generation Molten Car-
    bonate Systems," Vol. II, Project 8984 Final Report for
    1 July 1976 -30 September 1977, Institute for Gas Tech-
    nology, Chicago IL.

POTENTIAL FUEL CELL APPLICATION
IN THE METALLURGICAL INDUSTRIES

Malcolm S. Jones, Jr.
EBASCO Services Inc.
Santa Ana, CA 92704

There are a number of potential ways that fuel cells can be used in the metallurgical and metal working industries. One primary application in the metallurgical industry is for electrolytic reduction of oxides or chlorides. These processes are used for production of aluminum, magnesium, etc. Another use is electrolyte refining which is practiced in the copper industry. These applications require low voltage, high amperage direct current power supplies. Fuel cells appear to be well suited as electrical power sources for these industries. If cogeneration can be incorporated in these applications, high rates of return on investment can be projected.

Metal finishing operations such as plating, galvanizing, plasma spraying, etc., require direct current at modest power levels and, again, low impedances. Fuel cell power systems, which eliminate the need for rectification equipment, should be competitive for these applications and should be able to be controlled by simple mechanisms.

Electric arc furnaces which are used for melting in several industries require high current power supplies and operate intermittently. Inasmuch as the performance of the arc furnace is not sensitive to the wave shape of the supplied electrical power, and precise frequency control is usually not required, a fuel cell system could be coupled to an arc furnace or similar system, through a reasonably low cost power conversion device, which might make a fuel cell system attractive for these applications.

Many of the iron ore reduction processes, such as blast furnaces, produce substantial streams of hydrogen gas, or carbon monoxide which could be shifted to hydrogen. These waste gas streams, after suitable clean up, are potential fuels for fuel cell systems which can produce electrical power for other uses in the mill.

This broad spectrum of potential applcations will require fuel cell systems and components which may be somewhat different than those associated with the electrical utility industry fuel cell applications.

Fuel Cells in the Chlorate Industry - The Canadian Scene

I. H. Warren, Ph.D., P. Eng.

Chemetics International Company

Vancouver, British of Colombia, Canada

A review is presented of the Canadian chlorate industry
and the possibilities for the application of fuel cells.
The developments necessary to bring about large scale
application of fuel cells are considered together with
the economic limitations that will restrict their use.

FUEL CELLS FOR CHLOR-ALKALI PLANTS

J. M. Anderson   PPG Industries, Inc.
J. R. Joiner   Fluor Engineers and Constructors
H. C. Maru   Energy Research Corporation

An average of 2600 MW of direct current electricity were consumed in the United States in 1982 to produce 25000 tons per day of chlorine. However, 1982 was a poor year for the chlorine industry, with operating rates in the 65% range. By 1985 the DC power needs of the chlor-alkali market will probably increase to around 3200 MW.

While all of this DC power consumption represents a potential market for fuel cells, it is likely that the first installations will occur where especially advantageous situations exist. One of these might be the use of the hydrogen produced as a by-product of chlorine manufacture as the source of fuel for the fuel cells. Since the hydrogen generated could produce from 15% to 20% of the total DC power needs of a chlorine manufacturer, this represents one of the first areas where fuel cells might be employed. The size of this market should therefore be around 500 to 600 MW.

There are a number of favorable features of fuel cells which recommend their use to chlor-alkali producers as shown in Table 1.

TABLE 1

FAVORABLE FEATURES OF FUEL CELLS

A.	High Efficiency	40 - 50%
B.	D.C. Power	Produces D.C. power directly No rectifier losses
C.	Hydrogen Fuel	Could consume by-product hydrogen to produce 15% to 20% of the DC power needed.
D.	Reliable	Probably 95% availability
E.	By-Product Heat	Can produce 100 psi steam.
F.	Modular Design	Flexibility in sizing
G.	Non-Polluting	No ashes or obnoxious gases

A meeting of chlor-alkai representatives is scheduled in Denver on August 29, 1983 to discuss the formation of a potential users group. The results of this meeting will be reported.

Most of the chlorine producers are being polled as to the electrical characteristics of the fuel cell power source which they might individually install if fuel cells proved to be the economic choice. The results of this poll will be reported.

In order to match a fuel cell power supply to a chlorine cell circuit and to have an economical and reliable system a number of features of the power supply system will require further design and development. These are outlined in Table 2 following.

TABLE 2

ITEMS REQUIRING DESIGN AND DEVELOPMENT

A. Hydrogen fuel requirements
    1. Design for high utilization
    2. Required purity
        a. Chlorides
        b. Alkali

B. Air Purity
    1. Chlorides
    2. Alkali
    3. Particulates

C. Operating in parallel with Rectifiers
    1. Permissible Ripple in DC power
    2. Amperage control of the fuel cells
    3. DC circuit breakers

D. Operating as sole power source
    1. Voltage/Current control
        a. Switching out banks of fuel cells
        b. Increasing Oxygen partial pressure
        c. DC-DC controls

E. Waste Heat Utilization
    1. Steam generation
    2. Other uses

F. Performance vs. life using enriched air

G. Performance vs. life using pressure

H. Cost Studies

Solutions to these problem areas require the cooperation of potential
users, manufacturers, engineering and consulting firms, and agencies
such as the Department of Energy to work in concert. The Chlor-Alkali
section of the Potential Industrial Fuel Cell Users Group was formed
to aid in the dialogue between these parties and to facilitate fuel
cell development for our industry.

DEVELOPMENT OF FUEL CELL TECHNOLOGY
FOR INDUSTRIAL APPLICATIONS

H. Tajima
Fuji Electric Corporate Research and Development Ltd.
2-2-1, Nagasaka, Yokosuka, 240-01, Japan

H. Kaneko
Fuji Electric Company
1-1, Tanabeshinden, Kawasakiku, Kawasaki, 210, Japan

Introduction

Fuji Electric started research and development of fuel cell in 1961. We developed a 10 kw alkaline H_2/O_2 fuel cell for a shipboard in 1972 and a 2 kw alkaline H_2/Air fuel cell in 1977. The 2 kw fuel cell was incorporated into the power network model in Central Research Institute of Electric Power Industry to analyse the fuel cell performance in a transmission line. A 30 kw phosphoric acid fuel cell was developed in 1982 and has been operated at Sakaiko Power Station of the Kansai Electric Company Inc. under fully automatic control.

Recently, we are developing a 1 kw alkaline fuel cell unit aimed at using byproduct hydrogen, which will be completed by the end of 1983 and tested in 1984, under the contract with Agency of Industrial and Science Technology in Moonlight Project. Furthermore, a 1 MW scale PAFC power plant has being developed under the contract with New Energy Development Organization in Moonlight Project and will be tested by 1986.

R&D Efforts on Industrial Application

Chemical industry besides electric utility will be one of the biggest users of fuel cells because it has a large amount of byproduct fuel and also has techniques pertinent to operation of fuel cells. Fuji Electric has been making its effort on developing fuel cells for industry on the bases of above mentioned experience.

The most important problem to be solved, in order to realize a fuel cell for industry, is cost reduction of a fuel cell power plant. The power plant consists of many constituents such as fuel cell stacks, reactants supplier, power conditioner, control system and others. The cost of fuel cell stacks is now the highest of them. Therefore, Fuji Electric has set the target for developing low cost fuel cell stacks with the specifications shown in Table 1.

TABLE 1. THE SPECIFICATIONS OF LOW COST FUEL CELL STACKS

	Alkaline FC	PAFC
Voltage of cell	0.7 V/cell	0.65 V/cell
Current density	150 mA/cm^2	150 mA/cm^2
Operation temperature	65 °C	180 °C
Operation pressure	1 atm.	1 atm.
Fuel	CO_2 free H_2	Hydrogen rich gas
Oxidant	CO_2 free air	Air
Cooling method	Air	Air
Avtive electrode area	ca. 1000 cm^2	ca. 1500 cm^2

The active electrode area of alkaline fuel cell and PAFC are
selected apploximately at 1000 cm^2 and 1500 cm^2 respectively,
because these sizes are optimum to manufacture these cells
by applying our own existing techniques such as molding and
stamping suitable to massproduction. Such small sized cell
stacks have good replaceability which contributes to cost
reduction of the cell stacks.

Since the operation pressure of these two fuel cells is 1 atm,
we can simplify the structure of the cell stacks and easily
maintain the reactants leak rate within the design allowance
at such pressure.

Air cooling is adopted in both alkaline and acid fuel cells.
In the alkaline cell, air as oxidant, fuel and electrolyte
are circulated through the cell stacks to remove heat and
water genarated. The heat and water are then removed by air
cooling of these circulated fluids.

In PAFC, the cell stack houses the ribbed bipolar plates made
of molding the mixture of graphite powder and phenoric resin
but does not house any cooling plate, because the oxidant air
also works as coolant. Since large amount of air must be
supplied to cool the cell stack, evaporation loss of phospho-
ric acid becomes greater than other cooling methods. The loss
is decreased by operation at 180 °C. And the lost amount of
acid is automatically supplied by the acid supplier.

Summary

Consisting of above described small sized cells which operate at low pressure and low temperature, our fuel cell stacks have many advantages, namely, low cost, replaceability and maintainability.

Fuel cell having the characteristics which are almost the same as the specifications shown in Table 1 are now obtainable in our company.

The cost reduction problems of the cell stacks will be solved by development efforts. The cost target of the cell stacks is 200 to 300 $/kw.

But there remained some problems, including the reliability and the cost of the fuel cell power plant for industry. Because the plant consists of reactants supplier, power conditioner, control system and fuel cell stacks, all of them should be optimally designed. In this respect, cooperation with users is important in developing the fuel cell power plant for industry.

DEVELOPMENT OF PAFC SYSTEM AND
ITS APPLICATION TO INDUSTRIAL USE

K. KISHIDA, E. NISHIYAMA,   Y. HAMASAKI
Mitsubishi Electric Corp.   Mitsubishi Electric Corp.
Central Research Lab.   Kobe works
8-1-1 Tsukaguchi -Honmachi   1-1-2 Wadasaki-Cho Hyogo-ku
Amagasaki, 661, JAPAN   Kobe, 652, JAPAN

In order to establish the technology of phosphoric acid fuel cell power generating plants, Mitsubishi Electric had built a 50 KW experimental prototype plant (Mark-I) and operated it during the year 1982. Based on the operating experience of the Mark-I as well as the advancement of the cell and stack technologies, Mark-II, an advanced version of Mark-I, having higher module performance and elaborated system design was built in May 1983 and has been operated. Table 1 shows the Mark-II specification.

TABLE 1. SPECIFICATION OF 50 KW PAFC POWER SYSTEM
(MARK-II)

System
    AC Output   50KVA, 3 phase, 220V, 60Hz
    DC Output   55KW
    Fuel   Natural Gas
    Inverter Efficiency   91%
    Overall Efficiency   35%
    Control Scheme   Direct Digital Control

Fuel Cell Module
    Effective Reaction
      Area of a Cell $3,520 cm^2$
    Number of Cells   121
    Catalysts $1.05 \ mg/cm^2$
    Operating Temperature $190°C$
    Operating Pressure $3.5 \ kg/cm^2 \cdot G$
    Cooling Method   Water Cool
    Output   78.6V/704A
    Module Efficiency   51%
    Utilization Rates
      of Reactants   Fuel: 75% Air: 50%

Fuel Processor
    Process   Steam Reforming
    Reactors   Reformer
                          High Temperature CO Converter
                          Low Temperature CO Converter
    Steam-Carbon Ratio   4

The objective of our PAFC power system development is diversified. Grid connected electrical power generating plants are typical but industrial applications of fuel cells are of great interest as well. The fuel cells need hydregen and produce direct current. Chemical industries, particularly, are familiar with handling hydrogen and often use low voltage direct current, that is very likely to meet the essential nature of the fuel cells.

A study is being conducted on the application of a fuel cell system into a plant of petrochemical process where surplus hydrogen is avbailable (FIGURE 1). For the optimal system balance between the chemical plant process and the fuel cell system, a system survey and a conceptual design are being performed.

As to the direct current output of a fuel cell modul, dc-voltage control is the subject to be studied in the case of the use of direct current. "CHOPPER CONTROL" is the most reasonable method to meet various requirements possibly predictable in use of direct current to an industrial plant, for example, electrolytic process plant.

Aiming at these applications, testings are being conducted to verify the adaptability of the fuel cell system by use of our Mark-II plant.
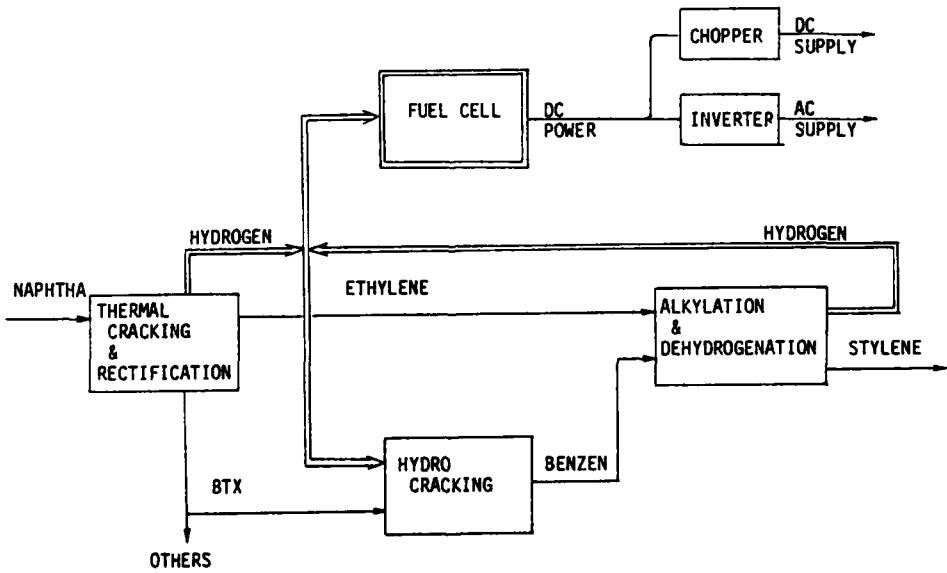

FIGURE 1. AN APPLICATION OF FUEL CELL POWER SYSTEM
TO PETROCHEMCAL PROCESS

OXY HYDROGEN-AIR FUEL CELL

ALVIN T. EMERY
Occidental Chemical Corporation
360 Rainbow Blvd. South
Niagara Falls, NY 14120

The OXY alkaline hydrogen-air fuel cell which is now in an advanced stage of development is specifically designed to overcome many of the cost-performance limitations of fuel cells to enable their consideration for a broader range of industrial applications. In particular, we believe the OXY Fuel Cell may have significant benefits for those manufacturing processes which are energy intensive and where large amounts of high purity hydrogen are available as a by-product of electro-chemical operations such as chlorine and chlorate manufacture.

The OXY Fuel Cell is based on concepts developed and refined by more than fifteen years of effort at Alsthom-Atlantique in France. A development program funded by Occidental and under its management was started in 1978 to take the basic Alsthom cell concepts and develop a commercial scale hydrogen-air fuel cell capable of meeting our cost and performance objectives. Up to the present time, most of the development work has taken place at the Massy laboratories of Alsthom.

The basic concept behind the OXY Fuel Cell is a low-cost high-performance configuration which is economical in size, weight, and manufacture. The cell makes maximum use of low-cost thermoplastics and conductive materials while avoiding the use of expensive engineering materials and complex methods of assembly. The unit incorporates a unique electrode structure which achieves high performance with minimum catalyst loadings. The OXY Fuel Cell with alkaline electrolyte is designed to produce low-cost electric power from pure by-product hydrogen where the hydrogen is ordinarily vented or burned in a conventional boiler to generate process steam. We believe the OXY Fuel Cell will be the lowest cost alkaline fuel cell technology available and will provide strong economic incentives for commercial use in plants having suitable sources of fuel.

The major advantage of the OXY Fuel Cell is its low cost and simple construction attributable to the use of conductive and non-conductive thin plastic components which can be produced and assembled on high speed automated production machinery.

The principal material of construction is polypropylene. Except for catalyst, the use of high-cost materials and complex configurations has been avoided.

Each unit cell contains a bipolar collector made from non-conductive and conductive polypropylene co-molded in a single operation. An anode is mounted on one side of the collector and a cathode on the other. A molded interframe positioned between the electrode/collector assemblies pro-

vides a chamber for the electrolyte. The inter-electrode gap is small to minimize internal resistance and power loss. The spatial arrangement of the cell components is shown in Figure 1.

FIGURE 1

EXPLODED TOP EDGE VIEW OF 2-CELL POLYSTACK
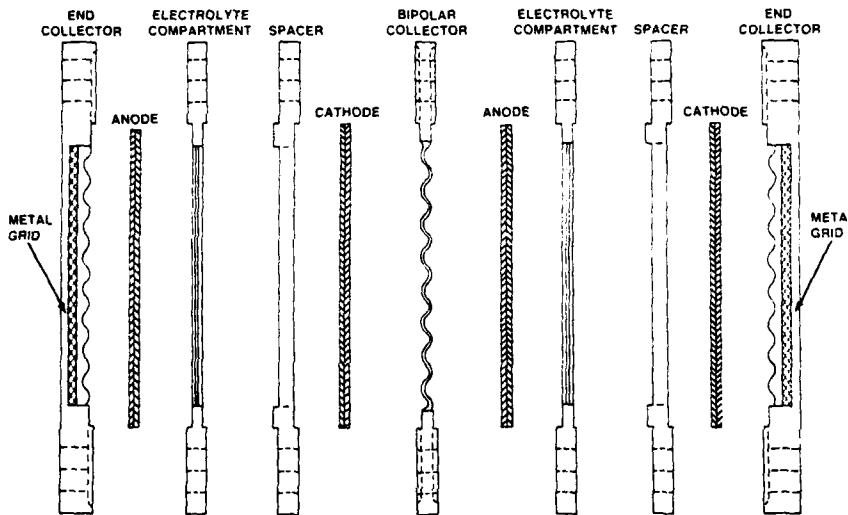
The following table shows typical performance characteristics of the OXY Fuel Cell at completion of the development program:

Current density . . . . 150 ma/cm^2
Unit cell voltage 0.80V
Cell efficiency 54%*
Power density . . . . 12.0 w/dm^2
Typical stack rating. . . . . . . 19 Kw (400 unit cells)
Cell temperature. . . . . 75°C
Electrolyte . . . . KOH or NaOH
Cell Life . . . . 8000 hours minimum

Figure 2 shows the expected voltage output of a unit cell over a range of current densities.

FIGURE 2

VOLTAGE VS. CURRENT DENSITY
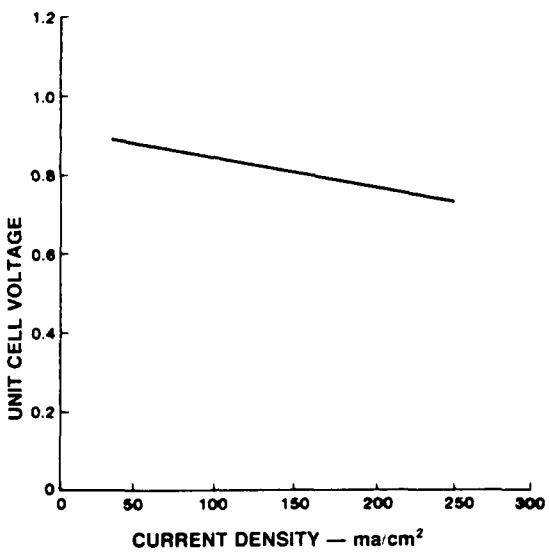
* Efficiency noted is based on higher heating
  value of hydrogen. Higher efficiencies can
  be achieved by operating at lower current
  densities.

Scale-up to the commercial electrode size of 4 dm^2 is
now complete.

Life tests on critical components have been under way for
several years. To date, anodes have passed 8000 hours life;
cathode tests are over 3000 hours and still progressing.
Life tests on multi-cell stacks, constructed from production-
line parts and assembled by techniques planned for the com-
mercial cell manufacturing plant are also underway.

The feasibility of high rate injection molding of the 1mm
thick 4 dm^2 scale components has been established. Figures
6 and 7 show major cell components made by injection molding.

Electrode manufacture using continuous calendering is a
well developed process.

FIGURE 3

MAJOR INJECTION MOLDED COMPONENTS
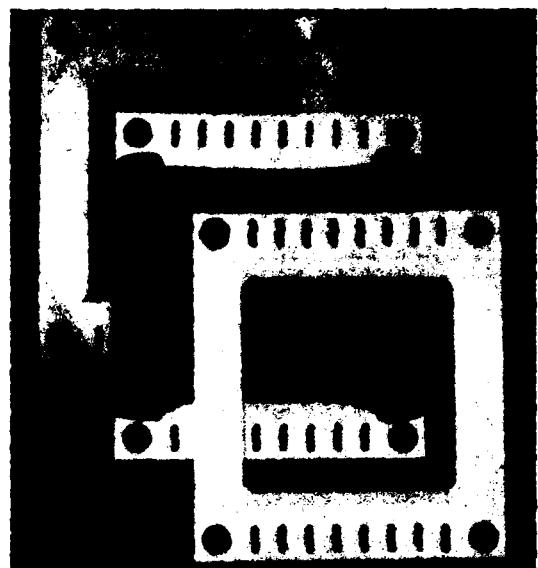
FIGURE 4

POLYSTACK CONTAINING 10
MONOELEMENT CELLS

In addition to the alkaline electrolyte system, work was started in early 1982 on the use of acid electrolytes using exactly the same components and configuration. Results to date have been extremely encouraging.

The acid system which can operate efficiently on hydrogen fuel can open up numerous areas of application outside of the Chlor-Alkali Industry. In addition, we believe that the cell life potential with acid electrolytes will be over 20,000 hours.

With automated mass production techniques at high volume component production, stack costs in 1983 dollars can be well under $100 per KW. The total system costs for the alkaline cell as used in chlor-alkali manufacturing plants will be in the range of $200 ~ $300 per KW.

The economic benefits of the hydrogen-air fuel cell derive from the higher value of the electric power generated compared to burning the hydrogen as a replacement for conventional fossil fuels in a steam boiler. The economic benefit obviously varies for the local situation depending on the cost of purchased electricity and the cost of boiler fuel.

For a fuel cell-chlorine cell coupling, the amount of electric power purchased can be reduced by about 625 K hr (ca. 25%) per short ton of chlorine by the use of the OXY Fuel Cell. The D.C. electricity requirements of the most technologically advanced membrane cell system can thereby be reduced from the range of 2200 KW hr per short ton of chlorine to under 1600 KW hr.

PERFORMANCE CHARACTERISTICS OF SOLID OXIDE FUEL CELLS

D. Q. Hoover, A. R. Jones
Westinghouse Electric Corporation
Pittsburgh, PA   15235

The Solid Oxide Fuel Cell (SOFC) has the following features which make it very attractive for industrial applications.

- High temperature by-product heat
- Fuel flexibility
- Simple supporting systems
- Low cost cell materials

These features are largely a direct result of the high operating temperature of the SOFC ($\sim$1800F) which, in turn, enables the use of solid state electrolytes. In addition, the SOFC has the desirable features of all fuel cells.

Figure 1 shows the DC power, high level heat and low level heat as a fraction of the fuel HHV produced by a typical SOFC generator as a function of cell operating voltage. Up to 35% of the HHV can be available at temperatures above 1200F. Even for applications where these temperature levels are not required, the size and cost of heat recovery equipment will be smaller than for lower temperature sources.

Figure 2 shows the profile of heat available as a function of temperature level for two SOFC operating conditions. The top temperature level shown is 1610F but this is a function of generator design. Temperature levels exceeding the cell operating temperature can be achieved by burning the spent fuel stream in the spent air stream and eliminating internal air preheat.

The SOFC can potentially use any gaseous fuel since it operates by oxygen ion transport (Figure 3) rather than fuel (or fuel related) ion transport and does not use poisonable precious metal catalyst. Experiments have shown that it operates equally well on dry or humidified hydrogen or carbon monoxide or mixtures of the two. There is no need for ancillary equipment to shift convert CO or recycle CO_2. The high temperature level operation enhances the feasibility of operating with in-situ reforming of gaseous hydrocarbons.

The materials used in SOFC can theoretically tolerate the impurities that are expected in gaseous fuels produced from coal. In the case of sulfur, which is one of the most worrisome, this has been verified by experiments(1). A 5% reduction of operating voltage resulted when 50 ppm of H_2S was added to a typical fuel composition. Apparently this caused no permanent damage since the cell recovered to its original performance when the sulfur addition was terminated.

Feduska and Isenberg give a brief history of the development of and the current technical status of the SOFC(1).

Acknowledgement

References

1. W. Feduska, A. O. Isenberg, "High-Temperature Solid Oxide Fuel Cell - Technical Status", Journal of Power Sources, Vol. 10, pp. 89-102, 1983.
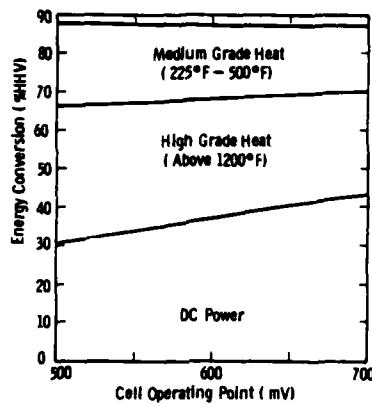
Fig. 1 – SOFC products at 85 % fuel utilization
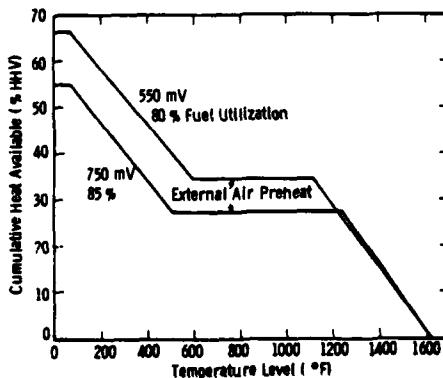
Fig. 2 – Temperature profile of available sensible heat
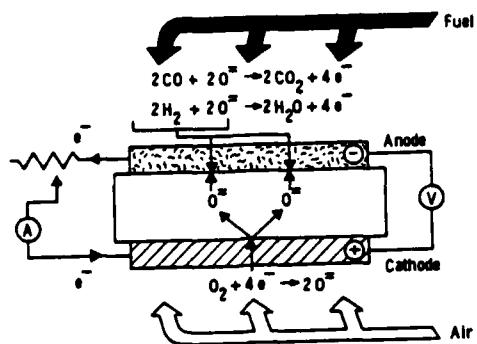
Fig. 3 — SOFC operating principle

GORDON LIU

POTENTIAL INDUSTRIAL FUEL CELL USERS GROUP (PIFCUG) BRIEFING

PIFCUG was initiated by a small group of potential industrial users at the National Fuel Cell Conference held in November, 1982. The objective of the group is to stimulate efforts in developing fuel cells for industrial needs. The group has grown to over 22 members; and the basic concept has won the endorsement of DOE, EPRI, GRI, IGT, TVA, and manufacturers both in the United States and overseas. The briefing will report the major accomplishments of the group.

NASA FUEL CELL APPLICATIONS FOR SPACE

Dean W. Sheibley
NASA Lewis Research Center
Cleveland, OH 44135

and
J. Dale Denais and Lynn S. Murgia
NASA Johnson Space Center
Houston, TX 77058

Introduction

Fuel cells continue to play a major role in manned spacecraft power generation. The Gemini and Apollo programs used fuel cell power plants as the primary source of mission electrical power, with batteries as the backup. The current NASA use for fuel cells is in the Orbiter program. Here, low temperature alkaline fuel cells provide all of the on-board power with no backup power source. Three power plants per shipset are utilized; each power plant contains two substacks connected in parallel.

One of the possible future applications for fuel cells will be for the proposed manned Space Station in low earth orbit (LEO)[1,2,3]. By integrating a water electrolysis capability with a fuel cell (a regenerative fuel cell system), a multikilowatt energy storage capability ranging from 25 kW to 250 kW can be achieved. Previous development work on fuel cell and electrolysis systems would tend to minimize the development cost of this energy storage system. Trade studies supporting initial Space Station concept development clearly show regenerative fuel cell (RFC) storage to be superior to nickel-cadmium and nickel-hydrogen batteries with regard to subsystem weight, flexibility in design, and integration with other spacecraft systems when compared for an initial station power level ranging from 60 kW to 75 kW. The possibility of scavanging residual O_2 and H_2 from the Shuttle external tank for use in fuel cells for producing power also exists.

A third area of interest is related to on-board power for future orbital transfer vehicles (OTV). With a space station in LEO and satellites in geosynchronous orbit (GEO), an OTV will become the next logical space vehicle. An OTV would be used to ferry equipment between LEO and GEO. Fuel cells are the prime candidate for electrical power on OTV's, since they are flight qualified and can operate using the boil-off from the cryogenic hydrogen and oxygen fuel used for propulsion.

Shuttle Fuel Cells

The Space Shuttle fuel cells continue to contribute to the success of the Space Shuttle missions.[4] On missions 5, 6, and 7, the fuel cells again performed flawlessly. The total power delivered during each of the flights was 1.89 megawatthours, 1.57 megawatthours, and 1.90 megawatthours, respectively. The average power level was 15 kW for flight 5 and 13 kW for flights 6 and 7.

107

The fuel cell performance on all flights has been better than was predicted from the qualification program. No performance degradation has been seen on any of the fuel cells. Fuel cell power plant 102 has accumulated the greatest amount of operating time; 757 hours.

The first three-substack fuel cells will fly on STS-9. All previous flights used two substacks per power plant. This change is being made to enhance the life and power capabilities of the fuel cell.

Through the alkaline fuel cell technology program, the fuel cells are being enhanced to produce a fuel cell with longer life and greater power capabilities for future Space Shuttle operations.

Regenerative Fuel Cell Feasibility Demonstrations

The feasibility demonstration of regenerative fuel cells is a combined program between Johnson Space Center (a mission center) and Lewis Research Center (a technology center). The program has focused upon improving fuel cell-electrolyzer component life and electrical efficiency. A 5-year (40,000 hour) life has been established as a goal with an overall electrical efficiency goal for the storage subsystem of 60% in a voltage range of 100 to 200 volts. Both the acid (SPE) and alkaline RFC systems are to be evaluated at JSC using breadboard test articles with periodic upgrading of component and system technology.

The acid breadboard was delivered to the Johnson Space Center on February 1, 1983. The breadboard consists of a fuel cell subsystem for power generation, an electrolysis subsystem for H_2-O_2 generation, a reactant storage subsystem, and a remote control console. The remote control console allows for individual operation of the fuel cell and electrolysis subsystems, operation of both subsystems simultaneously, and for the operation of the two subsystems in a cyclic mode. The remote control console also automatically monitors the subsystems and will shutdown the breadboard safely if any parameters go out of limits.

The initial objective of demonstrating the feasibility of using a RFC as an energy storage subsystem for a LEO energy storage system has been accomplished with the breadboard having accumulated 473 LEO cycles as of July 7, 1983. Several of these cycles have been acquired with the solar power station connected directly (no power conditioning equipment used) to the electrolysis subsystem. The LEO cycle consists of running the electrolysis subsystem for 54 minutes, and the fuel cell subsystem for 36 minutes. The electrolysis unit consists of 22 cells (0.23 ft^2) and operates at the following parameters; 24 amps, 36 volts, and 73° F. The gas is stored at 130 psia for the H_2 and 115 for the O_2. The fuel cell consists of eight cells (1.1 ft^2) operating at 112 amps, 6.5 volts, 160° F. The LEO cyclic mode is a closed loop operation.

The following findings have been observed about the acid system. No measurable water loss has been found, however, apparently four percent more gas is produced than is consumed. This is mostly due to the diffusion of the gases across the SPE membrane. Analysis of the gases produced and stored has revealed that the inerts are virtually gone (only 3 ppm of N_2 remains), and the hydrogen diffusing into the oxygen is increasing gradually (126 ppm H_2 in O_2 sample). There has been no permanent cell performance degradation detected in either the fuel cells or electrolysis cells. Also, the remote control console is working very well and is shutting the system down whenever tolerance limits are reached.

Future plans for the acid RFC breadboard include continued operation in the LEO cyclic mode, operation for 30 days of a scaled-down version of a Space Station power profile, and open-ended testing of both the fuel cell and electrolysis subsystems to establish a better endurance data base. The breadboard will also be utilized as a test bed for advanced cell and component development verification.

The alkaline RFC breadboard is scheduled for delivery at JSC in early January, 1984. It will integrate a 30 cell alkaline electrolysis unit (0.1 ft^2) with an Orbiter power plant (#708). The 30 cell electrolyzer unit (1.5 kW nominal) will be replaced in April, 1984 with a 6 cell 1 ft^2 electrolyzer unit (3 kW nominal) which is considered full size hardware for the space station mission. It also provides a better power match with the 4.5 kW Orbiter power plant.

The alkaline RFC is supported by endurance testing of the electrolyzer and fuel cell components. Electrolysis endurance testing has surpassed 22,000 hours (July, 1983) in the LEO regime with 0.1 ft^2 single cells at 180° F, 150 ASF, at ambient pressure with no voltage degradation.

A fuel cell stack of 6 cells (Orbiter-size hardware) has accumulated 6800 hours of LEO cycle endurance testing with a voltage degradation rate of less than 1 microvolt/hour. It is operating at 200 ASF and 140° F at 60 psia. A complete electrolysis subsystem including the controller is scheduled to begin a 20,000 hour endurance test in April, 1984.

Based on results of the breadboard testing, either the acid or alkaline RFC system will be selected for further development; a flight prototype engineering model system. This decision will be made in late 1984.

Orbital Transfer Vehicle Fuel Cells

The preliminary power requirements for an OTV have been identified as having a nominal range 0.5 kW to 2.0 kW, a peak power of 3.5 kW, operating at a nominal 28 volts, and an operating life requirement of 2500 hours. These requirements can be met with existing fuel cell technology. Orbiter technology can be down-sized to 0.25 ft^2 hardware and combined with flight-qualified ancillaries. A lightweight passive water removal design was demonstrated in the

late 1970's[5]. A lightweight fuel cell power plant definition program conducted by Marshall Space Flight Center based on Lewis Research Center technology demonstrated greater than 2500 hours within voltage regulation limits[6]. A 24-cell stack using passive water removal and edge current collection achieved 2000 hours of testing in 1980 under the Lewis program[7]. The lightweight system would require the development of new ancillary hardware.

Concluding Remarks

Fuel cells have found application in space since Gemini. Over the years technology advances have been factored into the mainstream hardware programs. Performance levels and service lives have been gradually improving. More recently, the storage application for fuel cell-electrolyzer combinations has been receiving considerable emphasis. The applications described here are part of a NASA Fuel Cell Program which has been developed to advance the fuel cell and electrolyzer technology required to satisfy the identified power generation and energy storage need of the Agency for space transportation and orbital applications to the year 2000.

References

1. "Electrochemical Cell Technology for Orbital Energy Storage", Contract NAS 9-15831, General Electric Direct Energy Conversion Programs, Report ECOES-12, November 19, 1979.

2. R. E. Martin, "Electrochemical Energy Storage for an Orbiting Space Station", Contract NAS 3-21293, United Technologies Corp., Report NASA CR-165436, December, 1981.

3. "Analysis of Regenerative Fuel Cells", Contract NAS 9-16151, Report D180-27160-1, Boeing Aerospace Co., August, 1982.

4. L. S. Murgia, "Space Shuttle Fuel Cell Performance", 1982 National Fuel Cell Seminar - Abstracts, p. 33-35.

5. B. Gitlow, W. Bell, and R. Martin, "Final Report - Strip Cell Test and Evaluation Program", Contract NAS3-20042, United Technologies Corp., Report NASA CR-159652, 1977.

6. R.E. Martin, "Final Report - Lightweight Fuel Cell Powerplant Components Program", Contract NAS 8-30637, United Technologies Corp. Report #FCR-1656, February, 1980.

7. R. E. Martin, "Final Report - Advanced Technology Lightweight Fuel Cell Program", Contract NAS 3-21293, United Technologies Corp., Report NASA-CR-165417, August 1980.

SMALL METHANOL POWERPLANT PROGRESS

S. Abens, M. Farooque, T. Schneider
Energy Research Corporation
3 Great Pasture Road
Danbury, CT 06810

Several small phosphoric acid fuel cell powerplants are currently under development at Energy Research Corporation. While several fuels may be considered as feasible, methanol presents the most attractive choice for the small powerplants.

Since it is a liquid at all ambient temperatures, methanol is easily transported and stored. It can be steam reformed at low temperatures (450-600°F) over a commercial shift catalyst using relatively simple, low cost equipment. Equally important, the bulk methanol of commerce is suitable for use in phosphoric acid fuel cells without costly pretreatment for impurity removal.

The basic methanol powerplant developed at Energy Research Corporation consists of an air cooled phosphoric acid fuel cell stack and a steam reformer for converting methanol to hydrogen and carbon dioxide. Water is supplied to the reformer along with the methanol in a mole ratio of 1.3 : 1 (equal to 58% methanol by weight). About 50% above stoichiometric fuel is delivered to the powerplant, the excess stack tailgas being used to provide the heat necessary for the reformer.

All powerplant development work at ERC is based on air cooled fuel cell stacks. The stack design in use until recently employed the cathode air stream for stack cooling. These stacks had the conventional cross flow, four manifold arrangement.

Currently, a modified stack design employing separate manifolding for the cooling air loop has been adopted. This arrangement, shown in Figure 1, allows low stoichiometric air flow through the cathode, which is important for water recovery from this stream. A separate cooling air stream is also necessary to ensure multiple restart capability for the powerplant when wet fuel combustion products are used to heat the stack.

Both stationary and transportable powerplants are currently under development at ERC. The most extensive development effort has been on transportable units for field use by the United States Army. These fuel cell powerplants are ruggedized for military service which requires frequent starting and operation with fully automatic control over a wide range of environmental conditions. The key performance requirements are availability, transportability, and quiet operation with minimum IR detectability. ERC delivered a 1.5 kW preprototype unit to the Army several years ago, and two 3 kW prototype units are scheduled for delivery by the end of 1983.

Figure 2 shows the schematic diagram for the Army 3 kW powerplant. Fast startup from any ambient temperature is obtained by the use of an auxiliary startup burner in addition to the normal run mode burner located in the reformer. This design will be shared by the 5 kW version of the powerplant also under development as part of the 3/5 kW powerplant program sponsored by U.S. Army MERADCOM.
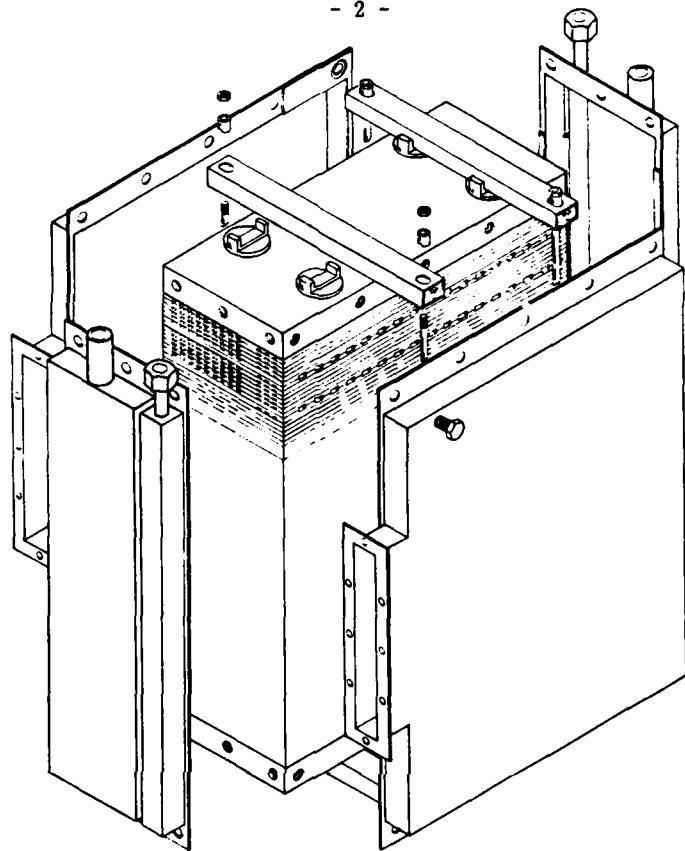
FIGURE 1   SEPARATE AIR COOLED STACK
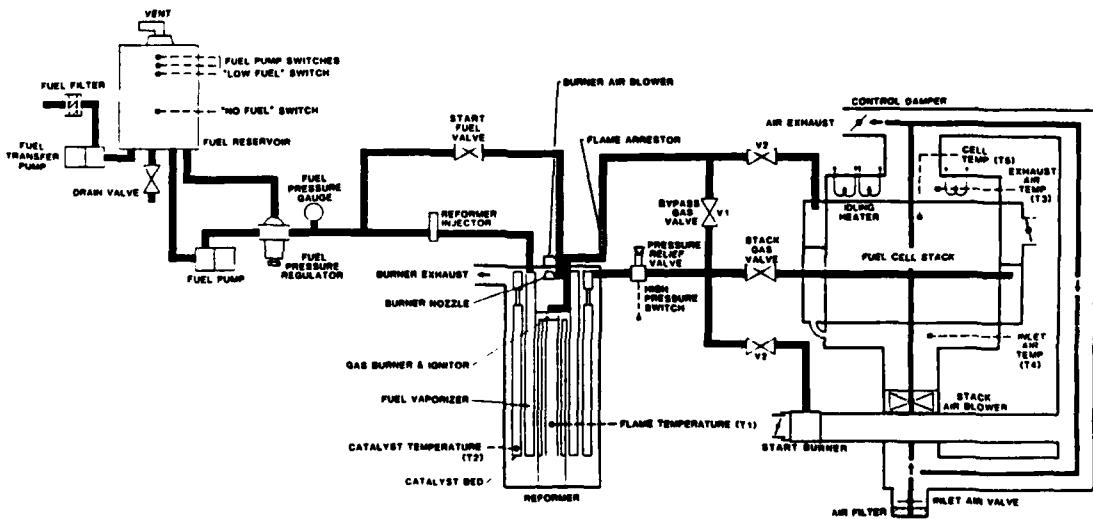

FIGURE 2   ARMY 3/5 kW POWERPLANT SCHEMATIC

A somewhat modified version of the Army 3/5 kW powerplant is under development for the United States Air Force. This 5 kW powerplant, intended for baseloaded stationary applications, is shown schematically in Figure 3. Because the installation of this powerplant may be at remote locations, minimum maintenance and low fuel consumption are the key requirements.
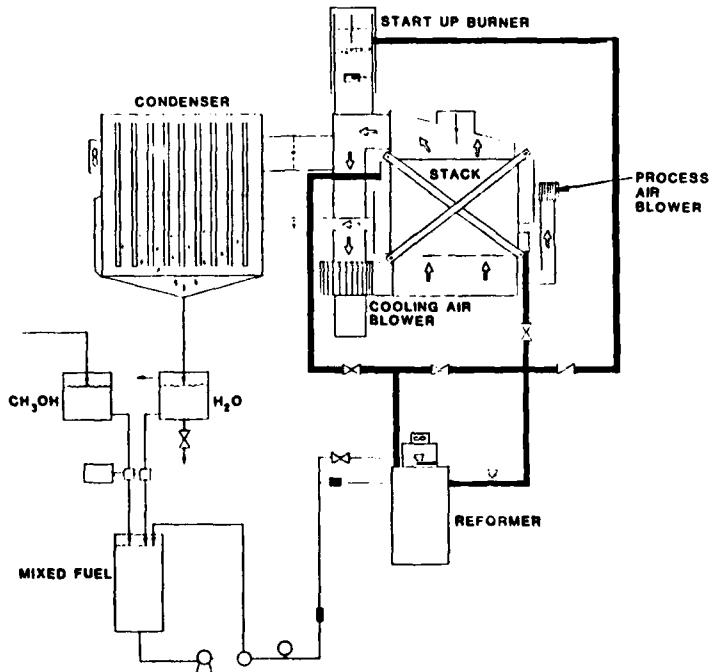

FIGURE 3   AIR FORCE 5 kW POWERPLANT SCHEMATIC

While the two powerplants share the basic component designs, the stationary unit will be built with internal water recovery capability because of the high cost of supplying fuel to the remote site. Water is recovered from the wet cathode exit gas by the use of a heat pipe condenser unit. The condensed water is collected in a holding tank and metered with the neat methanol into the mixed fuel tank. The 5 kW powerplant is scheduled for delivery to the Air Force in 1984.

A somewhat larger powerplant is under construction for the Los Alamos National Laboratories. This powerplant, also to be delivered in 1984, will have a nominal output of 20 kW with a 50% overload capability. In order to limit the height of the assembled unit to 36 in., two 100-cell stacks will be used as shown in Figure 4. This unit will be used to obtain baseline performance data with simulated vehicle loads.
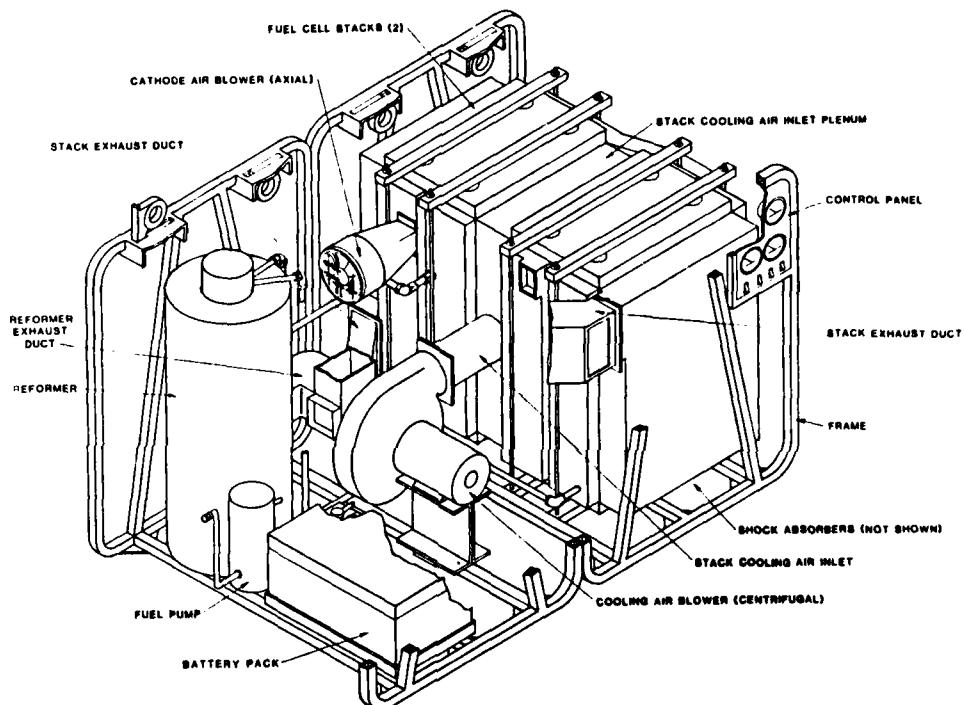

FIGURE 4   LOS ALAMOS 20 kW POWERPLANT

A FUEL CELL POWER SYSTEM
FOR FORKLIFT TRUCKS

M. J. Brand, J. J. Early, A. Kaufman,
A. Stawsky and J. Werth
Engelhard Industries Division
Engelhard Corporation
Iselin, N. J.   08830

Engelhard Industries is pleased to report the successful development of a fuel cell power system for forklift trucks. This liquid-fueled hybrid system has provided power for a 4000-pound-rated lift truck which has operated at an Engelhard plant for the past eight months. The system allows the advantages of an electric truck to be achieved but eliminates the need for battery recharging. Based on today's costs and with the present state of fuel cell technology, capital and operating cost savings can be achieved over conventional battery technology for forklift trucks.

In the mid 1970's, four of Engelhard's Model 750 fuel cell units, with additional cells to provide 1 kW output each, were provided to U.S. Army MERADCOM for use in their experimental forklift truck program. The MERADCOM-designed power system operated for several years using cylinders of compressed hydrogen to provide fuel. In 1980, MERADCOM replaced the hydrogen cylinders with metal-hydride tanks to provide greater on-board hydrogen-storage capacity. Engelhard supplied a 5 kW fuel cell stack with auxiliary components to provide the primary power for this system. Engelhard's most recent development of a fuel cell power system for forklift trucks provides for use of liquid methanol as fuel.

Technical Description

The system utilizes Engelhard's phosphoric acid fuel cell and methanol steam-reformer technologies. Methanol, stored in a fuel tank, is steam-reformed to hydrogen on board the truck. The fuel cell stack is sized to provide the average power needs of the truck; in the system currently being operated, the nominal fuel cell power is 4.3 kW. Four lead/acid auto-ignition type batteries are provided for peak power demands. During low-load operations, the batteries are recharged by the fuel cell stack. Hybrid operation allows the most efficient use of the inherently high energy density of the fuel cell system and the high power density and energy-interchange characteristics of the battery.

The fuel cell power system is capable of providing constant power output throughout a normal operating shift; a

major problem with battery systems is the loss of power
which occurs as the battery becomes discharged during mid-
shift. Unlike a battery, the fuel cell system can be re-
fueled with methanol in minutes. Emissions from the fuel
cell system are carbon dioxide, water vapor and heat, none
of which should cause problems in the warehouse environ-
ment where electric lift trucks are typically used.

The experimental system which has been built is designed
to demonstrate feasibility and functional performance.
For a production model, come reductions in system size
will have to be achieved; this can be achieved without ma-
jor technical obstacles. A drawing of the system as it is
conceived is shown in Figure 1.
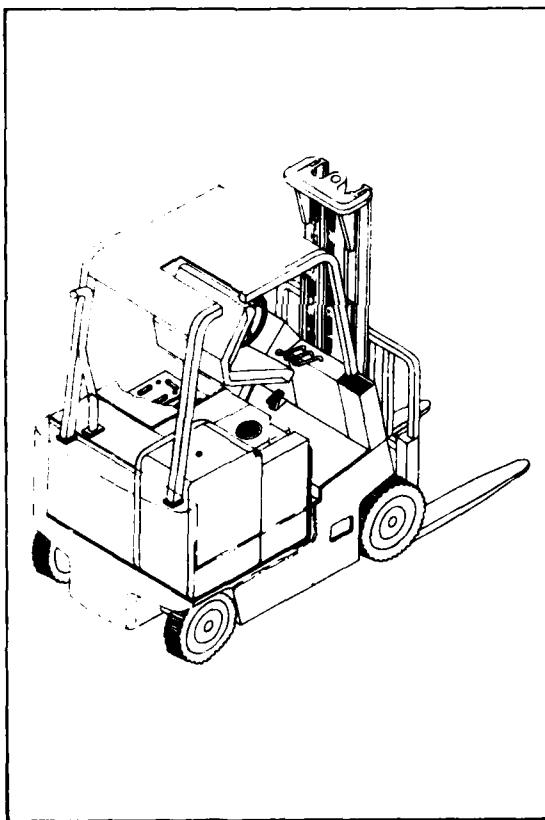
FIGURE 1
FUEL CELL POWER SYSTEM
Artist's drawing of a methanol fuel
cell power system installed in a
forklift truck.

Economic Case Study

Engelhard has conducted an economic analysis of the fuel cell power system for forklift trucks. A comparison was made between a conventional battery system and a methanol fuel cell hybrid system for powering a 5000-pound-rated lift truck. The analysis was made from the viewpoint of the user, who was assumed to be an industrial plant in New Jersey. Capital costs, operating costs and cumulative costs over a 10 year life-cycle were directly compared in constant dollars.

Major conclusions were:
1) Operating cost savings of 30% to 60% will be rea¹'zed with the fuel cell system, depending on the lucal cost of electricity.
2) Capital costs will be about 15% lower for the fuel cell system than for the battery/charger system.

117

CARBON MONOXIDE TOLERANT ANODES AND
FREEZE RESISTANT ELECTRODES

A. A. Adams, A. J. Coleman, and L. S. Joyce
U.S. Army Mobility Equipment Research
and Development Command
Fort Belvoir, Virginia 22060

Introduction

Tactical military fuel cell power units have several unique requirements which distinguish them from utility power plants. The power units are small (1.5 kW, 3 kW, and 5kW), and expected to endure numerous start-stop operations, and may be stored in severe climatic conditions (1). These indirect methanol/air fuel cells reform methanol to a hydrogen-rich stream which fuels an air-cooled stack. The technological program devoted to electrode development has focused on: (1) carbon monoxide tolerant electrocatalysts for fuel cell anodes to facilitate startup on reformer gas, and (2) the effect of thermal cycling on state-of-the-art electrodes to develop electrodes and shutdown modes for fuel cells cycled to sub-zero temperatures.

Carbon Monoxide Tolerant Anodes

It has been demonstrated that platinum-ruthenium alloys have good activity for the electrooxidation of hydrogen while exhibiting an improved tolerance for carbon monoxide when compared to platinum at low temperatures (2). Tungsten carbide also has shown excellent resistance to carbon monoxide poisoning (3) and with the addition of a small dispersion of platinum, good hydrogen activity (4).

Teflon bonded diffusion electrodes were made for each catalyst and used in both half-cell and single-cell experiments to obtain polarization and performance data as a function of temperature. Comparisons were made between: (a) a standard platinum fuel cell anode and 30 or 50 W% ruthenium-platinum alloy electrodes, (b) a tungsten carbide anode and tungsten carbide electrodes modified by the addition of 0.1 or 1W% platinum. The electrolyte was phosphoric acid and the reactants were pure hydrogen and a 3% carbon monoxide-hydrogen mixture. The electrodes' compositions and characteristics are summarized in Table 1. Surface areas were estimated from Transmission Electron Microscopy (TEM) data except for the Pt/WC sample. It was estimated from CO adsorption experiments and limiting current data that the platinum surface area was $7cm^2/cm^2$ geom and occupied approximately 30% of the WC surface.

TABLE 1

ELECTRODE CHARACTERISTICS

Electrocatalysts	Catalyst Loading (mg)	Surface Area (M^2/g)
Pt	0.5	140
Pt-Ru (50/50)	0.5	120
Pt-Ru (70/30)	0.5	---
WC	35	8
0.1% Pt/WCC	35	---
1.0% Pt/WC	35	---

The activities for the tungsten carbide systems are listed in Table 2. There was a modest gain in activity for the 0.1% Pt/WC electrode and a sizable gain for the 1% sample when H_2 was the reactant. When CO was present, the 1% sample lost 96% of its activity while the 0.1% sample decreased by 26% (5). This suggests that these loadings may be extremes and that by optimizing the platinum loading, a suitable electrode could be fabricated where the WC substrate would support the anode reaction at low temperature and the platinum become active as the temperature increased and faster reaction rates are required.

TABLE 2

COMPARISON OF THE ELECTROCHEMICAL ACTIVITY
OF WC AND 0.1% Pt/WC AT THREE TEMPERATURES IN 85%
PHOSPHORIC ACID

Temperature (°C)	Current Density at 0.15v (mA/cm^2 - geom)			
	H_2		3% CO-H_2	
	WC	Pt/WC	WC	Pt/WC
80	10.8	14.5	10.2	9.5
100	21.5	26.5	20.5	19.6
120	41.0	44.0	39.0	36.5
25*	2.6	89.8	2.6	3.4

*Data for 1% Pt/WC has a different structure than those above.

The anode polarization for platinum and platinum-ruthenium (50-50) electrocatalysts in the presence of carbon monoxide at various temperatures are compared in Figure 1. The advantages of using platinum-ruthenium at temperatures from 80-120°C in the presence of carbon monoxide is clearly
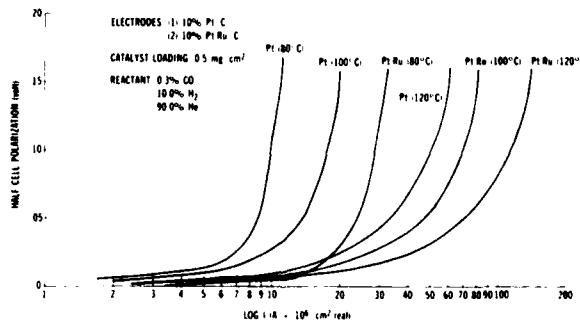

FIGURE 1

COMPARISON OF Pt AND Pt-Ru ALLOY POLARIZATIONS WITH
A H_2-CO MIXTURE IN 85% H_3PO_4 AS A FUNCTION OF TEMPERATURE

evident. Analysis of single cell data, summarized in Table 3, indicates little is to be gained by utilizing the alloy above 160°C, however, its superiority below 160°C as compared to platinum is demonstrated. Additional studies of ruthenium-platinum (30-70) alloy electrodes are in progress.

TABLE 3

SINGLE CELL PERFORMANCE FOR Pt and Pt-Ru ANODES

Temperature	E (volt) at $100 \ mA/cm^2$			
	H_2		$3\% \ CO-H_2$	
(°C)	Pt	Pt-Ru (50-50)	Pt	Pt-Ru (50-50)
180	0.626	0.664	0.625	0.656
170	0.613	0.652	0.608	0.636
160	0.597	0.635	0.582	0.612
150	0.580	0.622	0.533	0.576
140	0.559	0.606	0.359	0.464
135	0.546	0.595	0.125	0.390

These results indicate both platinum-ruthenium and platinum-tungsten carbide may be alternative anode electrocatalysts for fuel cells which are started below 150°C on reformate fuel.

Freeze Resistant Electrodes

It has been determined that the effect of shutdown of a fuel cell is dependent on the type of electrodes, electrolyte concentration, and mode of shutdown (6). Subscale (2"x2") phosphoric acid fuel cells using commercial and experimental carbon-supported platinum electrodes were subjected to operating conditions which simulate those in small mobile power unit applications. Single cells were cycled from an operating temperature of 180°C to -55°C using a variety of electrode types, cell configurations, operational modes and shutdown and startup procedures.

A typical cycling experiment involved the assembly of two identical 2"x2" cells which were run steady-state at 100 mA/cm^2 for a minimum of 72 hours. Once stable performance had been attained, diagnostic tests were performed including polarization curves to determine O_2 and H_2 gains and CO tolerance, and measurement of cell internal resistance and open circuit voltage. On-off and/or freeze-thaw cycling was then initiated on one of the cells while the other cell continued steady-state operation. Diagnostic tests were performed regularly on both cycled and noncycled cells to compare performances and detect possible cell component failures.

One of the objectives in this investigation has been to assess the effect of electrolyte concentration and volume on cell performance during temperature cycling experiments. Figure 2 shows typical performance losses at 100 ma/cm^2 for identically configured subscale cells which were tested in different modes. Cycling experiments were initiated after stable steady-state performance was reached. After each cycle or several cycles, the cells were returned to a period

of steady-state operation for diagnostic testing and perfor-
mance measurements to determine change from steady-state
performance prior to cycling. The first cell which was
cycled 100 times from operational temperature to -55°C, on
dry gases, with no electrolyte dilution showed a 14 mv loss
in performance on hydrogen-air. Cycling was continued on
the cell with a hold at 150°C (100 ma/cm^2) with the effect
of electrolyte dilution. As is evident, a change of slope
in performance loss is clearly demonstrated, in 18 cycles
the cell lost an additional 10 mv of performance. The
second cell exhibited a 26 mv loss in performance over 1000
hours of operation and 100 cycles to -55°C. The third cell
was run with humidified gases and performance losses after
two cycles were severe. This study emphasizes that dilution
of the electrolyte prior to shutdown and freezing causes
more severe performance deterioration than those suffered
when the phosphoric acid electrolyte is concentrated. The
electrode structure exhibiting the most resistance to per-
formance loss on freezing are those with the higher
hydrophobic characteristics.
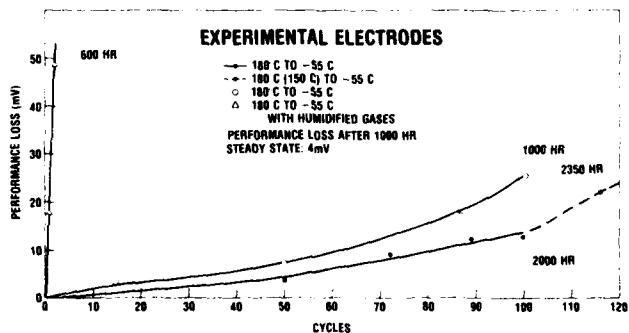
FIGURE 2

PERFORMANCE LOSS DUE TO THERMAL CYCLING

References

1. S. S. Kurpit, National Fuel Cell Seminar Abstracts
   168 (1982)

2. L. W. Niedrach, D.W. McKee, J. Paynter and I. F.
   Danziz, Electrochemical Technology, 5, 318 (1967)

3. H. Boehm and F. A. Pohl, J. Int des Piles à Combustile
   183-186 (Brussels, June 1969)

4. A. J. McAlister, L. H. Bennett, and M. I. Cohen,
   National Fuel Cell Seminar Abstracts. 116 (1980)

5. A. J. Coleman, A. A. Adams, J. A. Joebstl, and
   L. S. Joyce, 163rd Electrochemical Society Extended
   Abstracts. 1262 Abstract No. 848 (1983)

6. L. S. Joyce, J. A. Joebstl, A. A. Adams, A. J. Coleman,
   163rd Electrochemical Society Extended Abstracts.
   1260 Abstract No. 847 (1983)

ABSTRACT
STATUS OF SOLID POLYMER ELECTROLYTE FUEL CELL TECHNOLOGY

J.F. McElroy
General Electric Company
50 Fordham Road
Wilmington, MA   01887

Development effort in connection with SPE® fuel cell power-plants has been a continuing process at General Electric's Electrochemical Energy Conversion Programs (GE/EECP). The major current fuel cell developments include:

• A regenerative fuel cell for electrical energy storage in space vehicles utilizing the H_2O cycle.

• A methanol/air fuel cell powerplant for automotive applications.

• A high power density hydrogen/oxygen fuel cell powerplant for West Germany's Ministry of Defense.

• A regenerative fuel cell for electrical energy storage in mobile terrestrial applications utilizing the HBr cycle with complexed bromine.

Hydrogen/Oxygen Regenerative Fuel Cell

A regenerative SPE fuel cell utilizing the water cycle for space electrical energy storage has been under development since 1979 under NASA sponsorship. Currently a regenerative SPE fuel cell system is operating in "breadboard" configuration at NASA JSC. Several months of simulated low orbit operation have been accumulated on this system. In addition to the hydrogen/oxygen fuel cell a water electrolyzer subsystem is included in the regenerative fuel cell breadboard. The SPE electrolyzer cell design is identical to that developed for U.S. Navy and U.K. Royal Navy submarine oxygen generation plants.

While weight of earlier space fuel cell systems was of primary importance,in regenerative fuel cell systems for low earth orbit efficiency, life and low maintenance are of higher priority. The present SPE regenerative fuel cell breadboard system is demonstrating an energy storage efficiency in the 45 to 50% range. Work is in process to increase energy storage efficiency to ~60% and to reduce maintenance. Figure 1 shows the characteristics of the higher efficiency system.

OVERALL SYSTEM EFFICIENCY (%)

TOTAL SYSTEM WEIGHT (HUNDRED LBS.)

(15 MIL MEMBRANES @ 30/120 PSIA)

——————— CONSTANT ELECTROLYSIS CURRENT DENSITY, 50–200 ASF

– – – – – CONSTANT FUEL CELL CURRENT DENSITY, 10–60 ASF

39320 W   BUS POWER
180 V   BUS VOLTAGE
30 PSIA   F.C. OPER. PRESSURE
120 PSIA   E.C. OPER. PRESSURE
15 Mil   F.C & E.C. MEMBRANES
180°F   OPER. TEMPERATURE

FULL SOC DESIGN
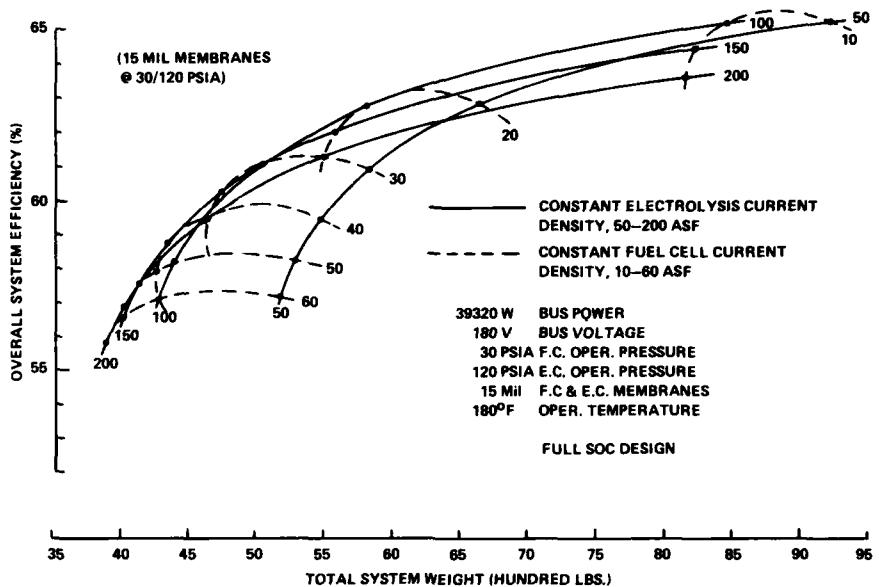
Figure 1.   Regenerative SPE H_2-O_2 Fuel Cell - System
            Efficiency Versus Weight

Methanol/Air Fuel Cell

Recent studies, sponsored by Los Alamos National Laboratory
LANL/DOE, have indicated that the SPE fuel cell powerplant,
fueled with methanol, can be competitive with other advanced
powerplants for potential automotive applications. Major
features of the SPE fuel cell powerplant concept include:

• Instant start up at ambient temperatures above 32°F

• No need for peaking batteries for acceleration

• High powerplant efficiency (50% HHV) at maximum continuous
  output rating

The selected SPE fuel cell characteristics for the automotive
application are displayed on Figure 2.

Currently work is continuing on the methanol fueled SPE fuel
cell powerplant under sponsorship of LANL/DOE. The primary
goals in the present effort are to:

• Identify and evaluate lower cost ion exchange membranes

• Optimize the anode catalyst for tolerance to CO in the fuel
  gas

• Reduce the amount of noble metal utilized in both anode and
 cathode catalysts

124
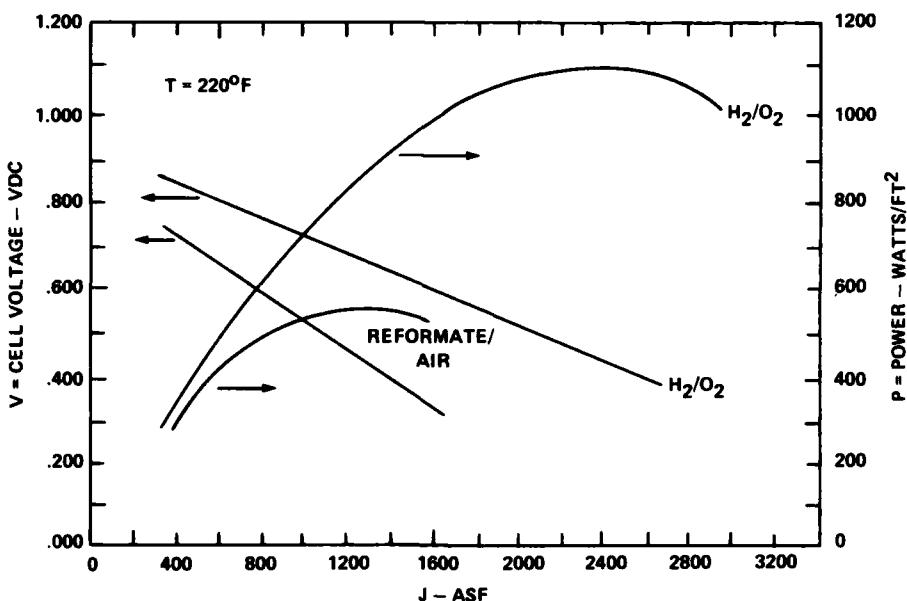
Figure 2. H₂/O₂ and Reformed Methanol/Air Performance
           Polarization Curves

In addition to potential alternative applications for which
this development program was initiated, consideration is now
also being given to the possibility for utilizing the meth-
anol/air SPE fuel cell powerplant for dispersed power genera-
tion. A consortium of companies is currently involved in this
consideration.

Hydrogen/Oxygen Fuel Cell

The hydrogen/oxygen SPE fuel cell is being developed for a
multi-megawatt powerplant for the West German Ministry of
Defense. Under a License Agreement with General Electric Co.,
Siemens AG of West Germany will be the eventual producer of
the SPE fuel cell hardware. Initial fuel cell samples have
been delivered to Siemens for their operational familiariza-
tion. These initial hardware sets include laboratory-sized
cells and full scale cells in short stacks.

Eventual multi-megawatt powerplants will be fashioned from a
multiplicity of 35 kW modules. These 35 kW modules will be
arranged in series and parallel to obtain the desired voltage
and current. The cells will be configured for continuous op-
eration at 500 amperes per square foot (ASF) while producing
350 watts per square foot. Figure 3 displays demonstrated
characteristics. Performance decay with time has been mea-
sured under the desired operating conditions to be <1.0 micro-
volt per cell hour at 100 ASF and <6.0 microvolt per cell
hour while operating continuously at 500 ASF.
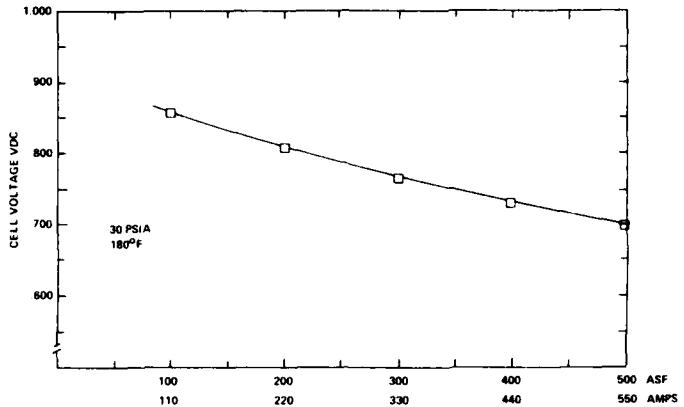
Figure 3. Build-up #1 Performance

Hydrogen/Bromine Regenerative Fuel Cell

High energy electrical energy storage efficiency (>75%) and
independent sizing for power and energy have been the major
advantages of the hydrogen/halogen SPE regenerative fuel cells.
The toxicity of the halogen reactant has in the past, been a
drawback for many applications. Under sponsorship of the U.S.
Army (MERADCOM) a bromine complex has been characterized which
essentially eliminates the toxicity concerns for the hydrogen/
bromine SPE regenerative fuel cell.

Preliminary cell tests utilizing the bromine complex indicate
some performance loss over the non-complexed bromine. (See
Figure 4.)
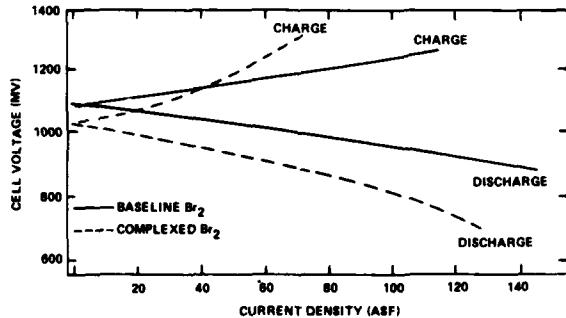
Figure 4. Regenerative SPE H_2-Br_2 Fuel Cell Performance

The current program with MERADCOM is directed toward electrode
optimizations to minimize the performance difference between
the complexed and uncomplexed bromine system.

ADVANCED ELECTROCATALYSTS AND SUPPORTS
FOR PHOSPHORIC ACID FUEL CELLS

V. Jalan, E.J. Taylor, D. Frost and B. Morriseau
Giner, Inc.
14 Spring Street
Waltham, MA 02154

I. Electrocatalysts

Improved activity and stability of the fuel cell cathode has been demonstrated by Jalan (1-4) using highly dispersed platinum alloys. It was found that some of these binary alloys, e.g. platinum-vanadium, were as much as five times more active than platinum, on a specific activity basis. Even so, at a current density of 200 mA/cm^2 this accounted for only 40 mV of the 400-500 mV lost as cathode polarization. Recent research at Giner, Inc. (NASA Contract DEN3-294) is directed towards understanding the factors affecting the oxygen reduction activity of platinum alloy electrocatalysts and extending the initial work on dispersed binary platinum alloys to ternary alloys of platinum.

Previously, increased performance and stability (lower rate of performance and surface area loss) had been demonstrated by CO treating and heat treating a standard platinum catalyst (5,6) as shown in Figure 1. The loss of performance with time of the CO treated and standard electrocatalysts is shown in Figure 2. Although these results had been confirmed (7), no explanation for the increased activity was presented. Recent x-ray diffraction analysis of the CO treated platinum reveals a lattice parameter contraction to 3.909Å (compared to 3.918Å for untreated platinum) and provides evidence for platinum carbide alloy formation (8). Although platinum carbide is not known to exist in bulk, Konig had observed it in thin film form (9) and very recently workers at the University of California also confirmed the existence of platinum carbide (10).

To date, a ternary platinum alloy catalyst (designated G82-5-10, patent application pending) supported on Vulcan XC-72 has exhibited a 50-60 mV oxygen reduction performance improvement at 200 mA/cm^2 in 100% H$_3$PO$_4$ at 200°C relative to a standard supported platinum catalyst of the same platinum loading (0.42 mg/cm^2). The oxygen reduction polarization behavior of this catalyst and a standard platinum catalyst is shown in Figure 3. On going work is concentrating on the determination of the long term stability of the alloy electrocatalysts in complete (2"x 2") fuel cells and on the development of supported platinum alloy electrocatalysts of even higher oxygen reduction activity and stability.

II. Electrocatalyst Supports

Although high surface area, electrically conductive carbon blacks have found widespread applications as catalyst supports for fuel cells, such carbon blacks do not always have adequate resistance to electrochemical oxidation (corrosion). Thermodynamically, carbon as a material is unstable at the cathode potential in hot

phosphoric acid. The kinetics of the electrochemical oxidation at the temperatures and potentials that are presently being used are sufficiently slow so that carbon can be practically used as a catalyst support, if the electrode potential is not allowed to get too high. Corrosion is not much of a problem at the anode because of the low potential, nevertheless, at cathode potentials corrosion adds to the various modes of fuel cell performance decay such as increased Pt migration due to undercutting (i.e., due to corrosion of the carbon under the catalyst), increased diffusion losses due to disruption of the carbon-Teflon interface (again due to corrosion of carbon at the interface) and puts a fundamental limitation on the lifetime of the fuel cell electrodes. Recent trends in acid fuel cell development such as higher operating temperatures and pressures, improved catalysts, and newer electrolytes, along with part load operation will increase the corrosion rate of the support. It is estimated that by increasing the cell temperature from $190^{\circ}C$ to $210^{\circ}C$ and the cell potential from 0.68 to 0.71V, the corrosion of the currently used carbon black support may increase by a factor of 3 to 4 (11). Clearly, more corrosion resistant materials than carbon or modified carbons will be required to offset the effects of higher cathode potentials resulting from increased operating temperatures and pressures.

An EPRI sponsored program (RP1200-8) is to identify and prepare materials which may be suitable support materials for advanced phosphoric acid fuel cells. An extensive screening program considered various transition metal silicides, nitrides and carbides and identified several candidate materials with potentially good corrosion resistance and electronic conductivity. One of the most promising candidates, a transition metal carbide has been prepared with specific surface areas up to 125 m^2/g. This material has exhibited excellent corrosion characteristics in initial screening and has been catalyzed with moderately dispersed platinum (23-90 m^2/g). This novel catalyst/support combination has been fabricated into gas diffusion electrodes (without optimization) and characterized for oxygen reduction. On a specific activity basis (see Figure 4), the novel catalyst/support combination exhibited an oxygen reduction activity five times higher than the standard. If this activity increase can be maintained in high surface area electrodes, a performance improvement of 60-70mV will be attained.

Future work at Giner, Inc. will concentrate on understanding the support preparation parameters and optimizing the electrode preparation parameters.

Acknowledgement

References

1. V. Jalan and D. Landsman, "Noble Metal-Refractory Metal Alloys as Catalysts and Methods for Making," U.S. Patent 4,186,110, Jan. 29, 1980.
2. V. Jalan, D. Landsman and J. Lee, "Electrochemical Cell Electrodes Incorporating Noble Metal-Base Metal Alloy Catalysts," U.S. Patent 4,192,907, March 11, 1980.
3. V. Jalan, "Noble Metal/Vanadium Alloy Catalyst and Method for Making," U.S. Patent 4,202,934, May 13, 1980.
4. V. Jalan, "Activity Enhancement of Platinum by Alloying With Base Metals," Extended Abstracts, Vol. 82-1, The Electrochem. Soc., Pennington, N.J., (1982), pp. 581-582.
5. V. Jalan and C.L. Bushnell, "Platinum Catalyst and Method for Making," U.S. Patent 4,137,373, Jan. 30, 1979.
6. V. Jalan, "Preparation of Highly Dispersed Platinum and Its Stabilization by Carbon," Extended Abstracts, Vol. 82-1, The Electrochem. Soc., Pennington, N.J. (1982), pp. 584-585.
7. R.J. Remick, "Stabilizing Platinum in Phosphoric Acid Fuel Cells," Final Report (Dec. 1980 - March 1982), NASA CR-10-5606, DOE/NASA/0208-4, July (1982).
8. V. Jalan and E.J. Taylor, "Importance of Interatomic Spacing in Catalytic Reduction of Oxygen in Phosphoric Acid," Extended Abstracts, Volume 83-1, The Electrochem. Soc., Pennington, N.J., (1983), to be published in Proceedings of the Symposium on the Physics and Chemistry of Electrocatalysts.
9. H. Konig, Naturierss, $\underline{38}$, 154(1951).
10. M.J. Whitcomb, U. Dahmen, and K.H. Westmacott, Acta Met., $\underline{31}$(5), 743-747(1983).
11. A.J. Appleby, "Some Material Aspects of the EPRI Acid Fuel Cell Program," National Fuel Cell Seminar Abstracts, Newport Beach, CA, Nov. 14-18, 1982.

References

1. V. Jalan and D. Landsman, "Noble Metal-Refractory Metal Alloys as Catalysts and Methods for Making," U.S. Patent 4,186,110, Jan. 29, 1980.
2. V. Jalan, D. Landsman and J. Lee, "Electrochemical Cell Electrodes Incorporating Noble Metal-Base Metal Alloy Catalysts," U.S. Patent 4,192,907, March 11, 1980.
3. V. Jalan, "Noble Metal/Vanadium Alloy Catalyst and Method for Making," U.S. Patent 4,202,934, May 13, 1980.
4. V. Jalan, "Activity Enhancement of Platinum by Alloying With Base Metals," Extended Abstracts, Vol. 82-1, The Electrochem. Soc., Pennington, N.J., (1982), pp. 581-582.
5. V. Jalan and C.L. Bushnell, "Platinum Catalyst and Method for Making," U.S. Patent 4,137,373, Jan. 30, 1979.
6. V. Jalan, "Preparation of Highly Dispersed Platinum and Its Stabilization by Carbon," Extended Abstracts, Vol. 82-1, The Electrochem. Soc., Pennington, N.J. (1982), pp. 584-585.
7. R.J. Remick, "Stabilizing Platinum in Phosphoric Acid Fuel Cells," Final Report (Dec. 1980 - March 1982), NASA CR-10-5606, DOE/NASA/0208-4, July (1982).
8. V. Jalan and E.J. Taylor, "Importance of Interatomic Spacing in Catalytic Reduction of Oxygen in Phosphoric Acid," Extended Abstracts, Volume 83-1, The Electrochem. Soc., Pennington, N.J., (1983), to be published in Proceedings of the Symposium on the Physics and Chemistry of Electrocatalysts.
9. H. Konig, Naturierss, $\underline{38}$, 154(1951).
10. M.J. Whitcomb, U. Dahmen, and K.H. Westmacott, Acta Met., $\underline{31}$(5), 743-747(1983).
11. A.J. Appleby, "Some Material Aspects of the EPRI Acid Fuel Cell Program," National Fuel Cell Seminar Abstracts, Newport Beach, CA, Nov. 14-18, 1982.

Figure 3. O_2 Reduction Activity for G82-5-10 and Pt.
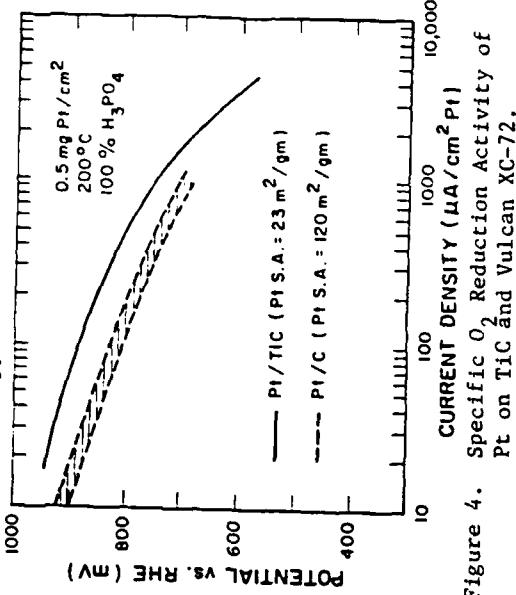
Figure 4. Specific O_2 Reduction Activity of Pt on TiC and Vulcan XC-72.


Figure 1. Schematic of "Carbiding" Process of Platinum Supported on Carbon Black.
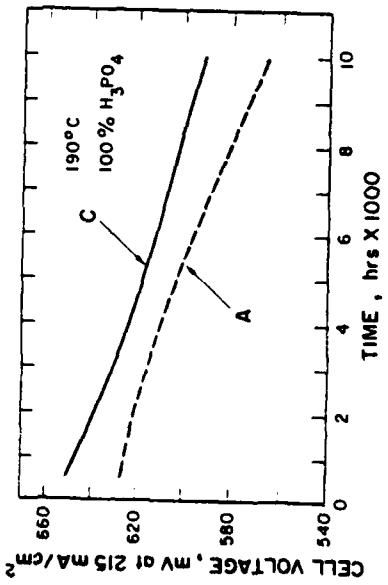
Figure 2. Cell Voltage vs Operating Time For Pt and Pt-C Supported on Carbon Black.

130

ELECTROCHEMICAL AND SURFACE SCIENCE RESEARCH ON FUEL CELLS*

S. Srinivasan, P. J. Hyde, A. Carubelli,[1] M. T. Paffett,
C. R. Derouin, R. E. Bobbett, C. T. Campbell, C. J. Maggiore,
T. N. Taylor, E. R. Gonzalez,[2] S. Gottesfeld,[3] S-M. Park,[4]
K-L. Hsueh,[5] H. Chang,[6] and D-T. Chin[7]

Los Alamos National Laboratory
P.O. Box 1663, MS D429

Los Alamos, NM 87545

1. Introduction

The objectives of the Los Alamos National Laboratory fuel cell research program, sponsored by the U.S. Department of Energy (Energy Storage Technology and Division of Fossil Fuel Utilization through the Morgantown Energy Technology Center and NASA Lewis Research Center) and the Los Alamos National Laboratory Institutional Scientific Research and Development Program, are to (i) study the effects of electrolytes (phosphoric and fluorinated sulfonic acids and solid polymer) on the electrode kinetics of fuel cell reactions; (ii) examine methods to minimize loading or find substitutes for the noble metals used as electrocatalysts in fuel cells; and (iii) investigate the stabilities of fuel cell component materials (electrocatalysts, supports, matrix, and bipolar plates). The research activities can be classified under the headings (i) Characterization of Electrode/Electrolyte Interfaces; (ii) Electrode Kinetics and Electrocatalysis of Fuel Cell Reactions (iii) Physiochemical Characterization of Electrolytes; (iv) Characterization of Electrodes; and (v) Evaluation of Fuel Cell Performance under Simulated Vehicle Operating Conditions. These investigations use capacitance, potentiostatic, galvanostatic, rotating ring-disk electrode, cyclic voltammetric, complex impedance, ion microprobe, ellipsometric, and infrared spectroscopic techniques. The major accomplishments in FY83 and some research plans for FY84 are summarized in the following sections.

2. Characterization of Electrode/Electrolyte Interfaces

2.1 Adsorption Behavior of $H_2PO_4^-$ and $CF_3SO_3^-$ Ions on Mercury

The adsorption behavior of anions from fuel cell electrolytes is important in elucidating the effects of this behavior on the electrode kinetics of the oxygen reduction reaction. The adsorption behavior of $H_2PO_4^-$ and $CF_3SO_3^-$ ions on mercury was analyzed from capacitance measurements in constant ionic strength and single salt aqueous electrolytes. Adsorption of $H_2PO_4^-$ and $CF_3SO_3^-$ ions on mercury is quite small. In the region of the potential of zero charge, $CF_3SO_3^-$ ions adsorb more than $H_2PO_4^-$ ions. The amounts adsorbed are greater from single salt than from constant ionic strength electrolytes. Specifically adsorbed ions competing with water dipoles for the electrode surface are due to the competition of the maxima in the plots of the specifically adsorbed charge versus electrode charge. The double layer structure and adsorption isotherms were analyzed according to the electrostatic model of the double layer.

2.2 Adsorption Behavior of $H_2PO_4^-$ and $CF_3SO_3^-$ Ions on Gold

Investigating the adsorption behavior of anions on platinum is more important than on gold because the former metal is to date the best electrocatalyst for acid electrolyte fuel cells. However, complications

arise in using capacitance techniques to obtain such information on platinum because of faradic reactions (adsorption/desorption reactions of hydrogen and oxygen) in the potential region of fuel cell reactions. Gold is ideally polarizable; therefore, it is more suitable for capacitance measurements and for obtaining adsorption characteristics of anions. Further, correlations can be drawn between adsorption behavior of anions ($H_2PO_4^-$, $CF_3SO_3^-$) and their influence on oxygen reduction kinetics on gold. Two types of experiments are planned to determine the former: (i) carry out the capacitance measurements on gold as they were done for mercury and (ii) use a kinetic probe method to gain insight on the double layer structure at the gold/electrolyte interface.

3. Electrode Kinetics and Electrocatalysis of Fuel Cell Reactions

3.1 Oxygen Reduction at Platinum in CF_3SO_3H

The kinetics of oxygen reduction at platinum in trifluoromethanesulfonic acid (TFMSA) (0.05 to 6.0 M) and in 1.0-M TFMSA containing small concentrations of phosphoric acid (0.003 to 0.1 M) were investigated using the rotating ring-disk electrode technique. In TFMSA, the oxygen reduction current on the oxide-covered platinum was smaller than that on the oxide-free platinum surface. This result is consistent with the greater amount of hydrogen peroxide produced on the oxide covered platinum. A reaction order of one-half with respect to the oxygen concentration for the oxygen reduction reaction was obtained from the ring-disk data. Addition of increasing amounts of phosphoric acid to TFMSA progressively decreased the oxygen reduction current and increased the reaction order with respect to oxygen. Because of these experimental results, the reaction mechanism proposed for the oxygen reduction on platinum in TFMSA is the fast dissociative adsorption of oxygen, followed by the first slow electron transfer step.

3.2 Oxygen Reduction at Gold in CF_3SO_3H and in H_2SO_4

Previous studies of oxygen reduction kinetics at gold show that the two-electron transfer reaction predominates, particularly in acid medium. Our study was to determine whether using the lesser anion adsorption of the $CF_3SO_3^-$ ion than of the HSO_4^- or SO_4^{2-} ions improves oxygen reduction kinetics in CF_3SO_3H over H_2SO_4. Therefore, rotating ring-disk electrode experiments were carried out on gold in CF_3SO_3H and in H_2SO_4 (concentrations 0.05, 0.1, and 0.25 N) at 25°C. Rate constants for the four- and two-electron transfer reduction reactions of O_2 and for the two-electron transfer reduction of H_2O_2 were calculated from the data obtained in these experiments. The cyclic voltammetric technique was used to characterize the gold electrode in these electrolytes. The specific adsorption of sulfate species inhibits the oxide formation on gold. The cyclic voltammograms indicate minimal adsorption of $CF_3SO_3^-$ ions. The results of the rotating ring-disk electrode experiments were consistent with the comparative adsorption characteristics of these ions, i.e., more H_2O_2 formed and faster oxygen reduction kinetics on gold in CF_3SO_3H than in H_2SO_4.

3.3 Combined Electrochemical and Surface Science Experiments to Investigate Effects of Foreign Adatoms on Fuel Cell Electrocatalysis

To model the effects of underpotential deposition (UPD) metals on the electrocatalysis of fuel cell reactions, the interactions of some simple molecules (H_2, CO, O_2) with a Pt (III) surface containing submonolayer coverages of vapor-deposited Cu are being investigated. The effect of the Cu overlayers on the adsorption and desorption of these species from Pt (111) will be characterized by low-energy electron diffraction (LEED), Auger electron spectroscopy

(AES), and thermal desorption spectroscopy (TDS). The results will be correlated with cyclic voltammograms and hydrogen ionization kinetics on Pt electrodes containing UPD Cu atoms.

4. Characterization of Electrodes

4.1 Ion Microprobe Investigation of Spatial Distribution and Stability of Electrocatalysts in Fuel Cell Electrodes

The usefulness of the ion microprobe technique for the analysis of electrocatalyst (platinum and other component) distribution in fuel cell electrodes was demonstrated in FY81 and FY82. Efforts are being made to apply this technique to the in situ examination of electrodes during electrochemical reactions. A vacuum-tight electrochemical cell has been designed and tested. It will be used with the ion beam microprobe to (i) investigate the extent of partial charge transfer during UPD of metals and the stability of UPD metals; (ii) measure CO adsorption on Pt and Pt alloys; and (iii) determine alloy and intermetallic electrocatalyst stabilities and changes in surface composition during electrochemical reaction.

4.2 Computer-Operated Automatic Ellipsometric Technique for Determination of Anion Adsorption on Platinum

Work with the ellipsometer in the past year has been directed at two subjects: the elucidation of a novel feature in the adsorption of bromide at a platinum surface and the adsorption of anions on platinum from solutions containing phosphate or trifluoromethanesulfonate species. When a platinum electrode is subjected to potential pulsing in a dilute solution of bromide ions (50 μM), the optical response shows slow diffusion of bromide ions to the surface. As the concentration of bromide in the solution is increased (0.1 - 2 mM), a fast transient response is due to the charging of the metal and the double layer. The trailing edge of the response, however, is apparently due to the reconstruction of the platinum surface as adsorbed bromide ions penetrate the platinum lattice. This reconstruction causes a positive shift in the optical parameters, which is unusual in film formation. These findings correlate well with similar findings for gas phase measurements. Anionic adsorption from both dilute and concentrated solutions of the phosphoric acid has also been studied using the ellipsometer. The feature previously reported to be associated with the densification of water in the double layer was also found in the optical measurements for solutions of phosphoric acid, ranging from 5% to 100% in concentration. This finding suggests that although the phosphoric acid is intimately associated with the surface of the platinum electrode, it does not interact with the surface. Measurements made with smaller concentrations of phosphoric acid (2 - 5 mM) in a background of 0.1 M perchloric acid show a clear adsorption effect of a phosphate species on the platinum surface. The potentials at which the adsorption begins on platinum (as seen in the measured ψ and Δ curves) suggest strongly that the adsorbing species is the monobasic phosphate anion rather than the neutral molecule.

4.3 Electromodulated Infrared Spectroscopic Technique for Examination of Chemisorbed Species on Electrodes

An electromodulated infrared spectroscopic method is being developed to investigate changes in chemisorption of ionic and neutral species (reactants, intermediates, products, solvent, electrolyte) on electrodes upon variation of the potential across the electrode/electrolyte interfaces. The technique employs phase-locked detection of reflected monochromatic light beams from the electrode surface while the potential is modulated between two values to cause periodic change in

chemical environments at the electrode surface. Efforts are under way to investigate (i) the adsorption of species on platinum from concentrated phosphoric acid and (ii) the mechanisms of CO poisoning and inhibition.

5. Evaluation of Fuel Cell (Single Cell) Performance under Simulated Vehicle Operating Conditions

Achievements in the effort to optimize single cell design and operating conditions include measurement of the long-term performance under steady-state operating conditions, design and testing of electronic circuits for IR-free measurements in proposed pulsing experiments, and data acquisition and reduction. A bank of six independently controlled single cells is being set up to investigate the time variation of performance as a result of load changes. Frequency, duty cycle, and impedance changes encountered by fuel cell power plants in electric vehicles will be simulated.

References and Notes

1. Guest Scientist at Los Alamos National Laboratory (January 1982 - December 1983), supported by CNPq Brazil, carrying out research for Ph.D. degree in Chemistry from Instituto de Fisica e Quimica de Sao Carlos, USP, Brazil.
2. Visiting Scientist at Los Alamos National Laboratory (May - July 1983) from Instituto de Fisica e Quimica de Sao Carlos, USP, Brazil.
3. Visiting Scientist at Los Alamos National Laboratory (July - September 1983) from Department of Chemistry, Tel Aviv University, Israel.
4. Consultant from Department of Chemistry, University of New Mexico, Albuquerque, NM 87131.
5. Junior Research Associate at Los Alamos National Laboratory (May 1981 - August 1982). Research work at Los Alamos toward Ph.D. degree in Chemical Engineering from Clarkson College, Potsdam, NY 13676.
6. Graduate Student at Los Alamos National Laboratory (May - August 1982) from Department of Chemical Engineering, Clarkson College, Potsdam, NY 13676.
7. Consultant from Department of Chemical Engineering, Clarkson College, Potsdam, NY 13676.

CARBON CORROSION IN HOT PHOSPHORIC ACID FUEL CELLS

Paul Stonehart and Joy P. MacDonald

Stonehart Associates
Madison, CT 06443, U.S.A.

Platinum-based electrocatalysts are used to accelerate hydrogen oxidation and oxygen reduction to produce electricity in hot phosphoric acid fuel cells. In order to increase the fuel cell reaction rates, the operating temperatures have been raised from 135°C to 160°C and now to 210°C. This has caused metallurgical sintering of the metal electrocatalyst with consequent loss of surface area as well as densification and cracking of porous electrodes. Supporting the active electrocatalyst particles on a high-surface area carbon has overcome the electrode densification and cracking problems and reduced the rate of loss of electrocatalyst surface area. In addition, the use of the carbon support has increased dispersion of the metal electrocatalyst to improve the utilization.

In hot phosphoric acid at cathodic potentials, the carbon surface is capable of being oxidized, and the degree of oxidation will depend on the carbon precursor as well as the pre-treatment of the carbon. Two important parameters govern the primary oxidation rate for any given carbon in an electrochemical environment: the electrode potential (the carbon corrosion is an electrochemical process and therefore will increase rapidly as the electrode potential is raised) and temperature.

If it is considered that the electrochemical corrosion of carbon electro-catalyst supports in phosphoric acid proceeds through the formation of carbon surface oxides at preferred sites, then these sites would be at edges, dislocations, and discontinuities in the layer planes of the microcrystalline carbons. Reactive sites (usually referred to as unsaturated sites) have been identified previously (1). It is thought that once an unsaturated site has been formed, continuous propagation of the carbon corrosion (oxidation) will proceed until the crystallite orientation has been consumed. The review by Thomas (2) deals with dislocations in the oxidation of graphitic carbons. Thomas points out that basal dislocations do not influence the oxidation but non-basal dislocations are inextricably associated with "active sites" in oxidation at the basal surfaces.

Heckman and Harling (3) examined the gas-phase oxidation of carbon black microstructures by electron microscopy. Electron micrographs showed that normal thermal and furnace blacks generally oxidize from the inside out, forming capsules. The particle dimensions do not change until the capsules collapse. Graphitized thermal blacks oxidize from the outside in with concomitant loss in particle dimensions. This gave rise to a new "concentric crystallite" model of carbon black microstructure.

Simple treatments such as heating the carbon in steam or in oxidizing environments change the surface structure. In this way, reactive end-groups would be removed and pores or dislocations in the carbon surface enlarged (4).

The introduction of boron substitutionally in the carbon lattice has been shown by several workers (5,6,7,8) to lower the Fermi level of the carbon. The boron acts as an electron acceptor and can enter the graphite lattice by substituting for the carbon at trigonal sites. It is possible that the doping of carbon with boron would provide "trap sites" for the platinum crystallites.

Since Vulcan has been well-characterized, it was chosen as the carbon for the doping experiments. The general effects of temperature and potential on the corrosion rate of Vulcan XC-72R described above were found to apply to all of the carbons studied in this program. Actual corrosion rates varied greatly with the type of carbon and a change in the corrosion rate with time also varied with the carbon type.

While the corrosion experiments were run, Tafel slopes (dE/dlog i) were obtained on the carbons at differing times. It was found that, in general, the Tafel slopes became more acute as the carbon was removed. (The value of dE/dlog i became less). In addition, the Tafel slopes differed according to the type of carbon and the history of the carbons. Log corrosion currents versus log time plots were not linear at short times but were more linear for the carbons with more highly ordered surfaces.

As mentioned above, Vulcan XC-72R was chosen as the carbon for the initial experiments for doping with boron. BET surface areas were measured for heat-treated samples of both Vulcan and boron-doped Vulcan as a function of heat treatment temperature. It is evident that the addition of boron has an effect beyond that of heat-treatment alone. Corrosion characteristics were studied to determine the stabilities of the doped carbons as cathode substrates for hot phosphoric acid fuel cell applications. Electrodes fabricated from the heat-treated boron-doped Vulcan samples mixed with PTFE were held at 1.0V in both $165^{\circ}C$ and $200^{\circ}C$ H_3PO_4.

The corrosion currents for boron doped carbons support the trend of other characteristics, which suggest that $1600^{\circ}C$ is the heat-treatment temperature above which no significant additional benefit is obtained. Based on the Tafel slope for the carbon corrosion reaction, there is a fairly steady improvement with increased heat treatment temperature from $1000-1600^{\circ}C$. In addition to the change in Tafel slopes with heat treatment temperatures up to $1600^{\circ}C$, the Tafel slope at 1000 minutes had a very low value at each test temperature and remained essentially unchanged during the duration of the test. This implies that not only the surface, but the underlying structure of the carbon has been stablized. The Tafel slopes for the $1600^{\circ}C$ heat-treated, boron-doped Vulcan are lower than that for the $2500^{\circ}C$ heat-treated Vulcan, which is a significant finding. Lowered Tafel slopes have been associated with enhanced stability. According to Marchand (9), after the boron has

136

been added to the carbons, a subsequent heat treatment at 1700°C or above allows the diffusion of the foreign atoms into the carbon and their substitution at trigonal sites.
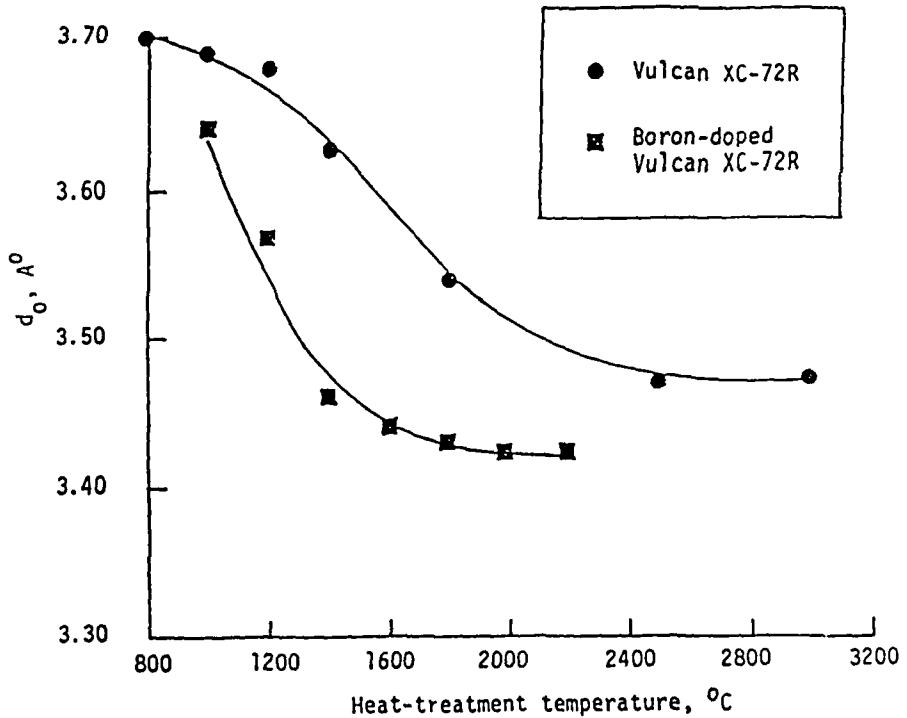

Figure 1: d_o vs. heat-treatment temperature for heat-treated Vulcan XC-72R and heat-treated boron-doped Vulcan XC-72R.

X-Ray diffraction parameters were measured for the heat-treated, boron-doped Vulcan samples. Values for d_o are plotted as a function of heat-treatment temperature in Figure 1, with the values for undoped heat treated Vulcan included for comparison. The addition of the boron is seen to have an effect beyond that of the heat treatment alone. This effect has been observed by other workers and could be interpreted as being indicative of enhanced "graphitization"; however, Maillard and Maire (10) caution against the use of lattice parameters exclusively to determine the degree of graphitization. According to Turnbull et al (11), the boron-carbon bonds for the substitutional atoms give rise to a c parameter contraction. The depression of d_o values for the heat-treated boron-doped Vulcan XC-72R samples cannot be interpreted as conclusive evidence that the boron-doping has resulted in more 'graphitic' character.

The clustering of the Tafel slopes for the heat-treated boron-doped Vulcans at values lower than obtained for Vulcan heat-treated at 2500°C (Figure 2) supports the conclusion of enhanced stability, which is

loosely associated with the extent of "graphitization". In Figure 3, BET surface areas are plotted versus d_o for the heat-treated, boron-doped Vulcan samples.

It suggests that the boron-doped Vulcan heat treated at 1600° has a more graphitic character (from its low value of d_o, supported by the corrosion characteristics) yet retains a higher BET surface area than Vulcan heat-treated at 3000°, which is indeed a signficant result. Generally speaking, the higher the surface area of the substrate, the greater the surface area of the noble metal that can be supported on it. Thus, the boron-doping theoretically allows more efficient utilization of the noble metal electrocatalyst on a more stable support, even without the consideration of the introduction of trap sites.

REFERENCES

1. B. R. Puri, J. **Indian Chem. Soc.** 51, 62 (1974).
2. J. M. Thomas, "Enhanced Reactivity at Dislocations in Solids" in "Advances in Catalysis", Academic Press,NY.19, 293 (1969).
3. F. A. Heckman and D. F. Harling, **Rubber Chemistry and Technology** 39, 1 (1966).
4. J. M. Thomas, E. L. Evans and J. O. Williams, **Proc. Roy. Soc.** A 331, 417 (1972).
5. C.A. Klein "Chemistry and Physics of Carbon" (Ed. P. L. Walker, Jr.) 2, Marcel Dekker, New York, 225 (1966).
6. R. Gremion, F. Tombrel, J. Maire and J. Mering, **Compt. Rend,** 260, 1402, (1965).
7. P. Delhaes and A. Marchand, **Carbon** 3, 115 (1965).
8. J. Zanchetta, P. Belougne and H. Gasparoux, Paper EP-11, 9th Conference on Carbon, Boston (1969).
9. A. Marchand "Chemistry and Physics of Carbon" (Ed.P. L. Walker, Jr.) 7, Marcel Dekkar, New York 155 (1971).
10. P. Maillard and J. Maire, **Compt. Rend.** 267, 436 (1968).
11. J. A. Turnbull, M. S. Stagg and W. T. Eeles, **Carbon** 3, 387 (1966).
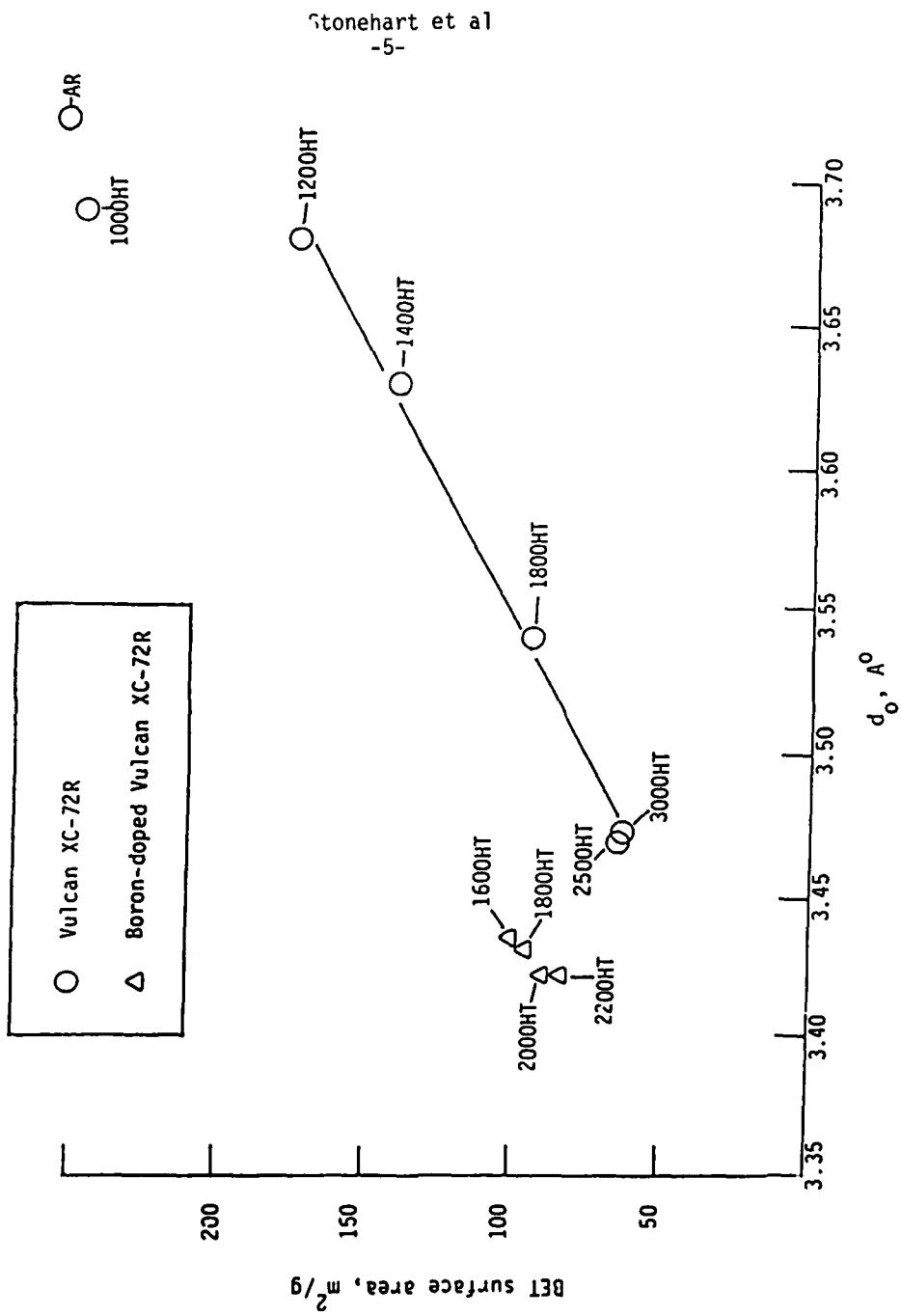
Figure 3: BET surface areas vs. d_o for heat-treated Vulcan XC-72R and heat-treated boron-doped Vulcan XC-72R.
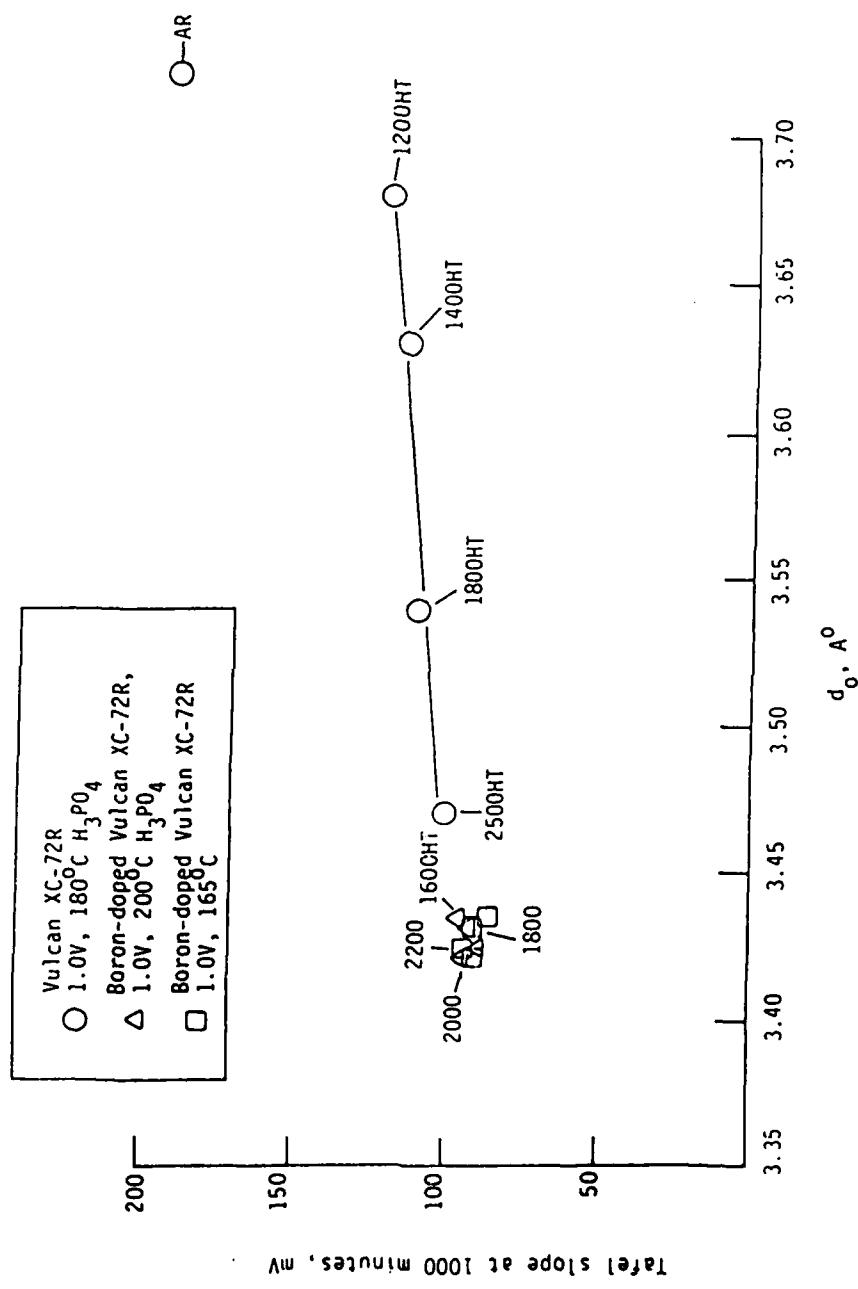
Figure 2: Tafel slopes at 1000 min. vs. d_o for heat-treated Vulcan XC-72R and heat-treated boron-doped Vulcan XC-72R.

ADVANCED ELECTROLYTES FOR
ACID FUEL CELLS: AN OVERVIEW

Philip N. Ross, Jr.
Lawrence Berkeley Laboratory
Materials and Molecular Research Division
University of California
Berkeley, CA 94720

It has been demonstrated in a number of investigations that
the kinetics of oxygen reduction on Pt are significantly
higher in trifluoromethane sulfonic acid (TFMSA) solutions
than in phosphoric acid (1-3). These differences appear to
be due to the higher oxygen solubility and the lower specific
adsorption of anions in TFMSA (4). However, the further in-
vestigation of TFMSA as a fuel cell electrolyte has revealed
the undesirable physical properties of this material that may
limit its usefulness. TFMSA solutions more concentrated than
ca. 7 M have wetting contact angles on polytetrafluoroethy-
lene (PTFE) surfaces, ionic conductivities lower than desire-
able, and high acid vapor pressure (5). The wetting of PTFE
causes loss of the hydrophobic gas-diffusion electrode struc-
ture essential for low transport losses at high current den-
sity, and the high vapor pressure represents a life limitation
and/or maintenance problem. Pure hydrogen-air fuel cells us-
ing 6 M TFMSA at 60°C have shown improved performance relative
to state-of-the-art phosphoric acid fuel cells, but use with
hydrogen containing carbon monoxide at levels above ca. 0.01%
severely poisons the Pt electrode at such a low temperature
(6). Use of less volatile higher homologs of TFMSA was sug-
gested by Baker and co-workers (7), particularly the dimeric
form of TFMSA, tetrafluoroethane -1,2- disulfonic acid
(TFEDSA). A number of research groups have pursued this idea
in recent years as part of the MERADCOM, DOE and EPRI fuel
cell development programs. Progress has been slow due to the
difficulty in synthesizing the higher homologs of TFMSA but
within the last two years both ECO and Case Western Reserve
University (CWRU) have succeeded in synthesizing TFEDSA
and CWRU has synthesized difluoromethane disulfonic acid
(DFMSA). The physical properties of these new acids are about
what one would expect by intuitive extrapolation of the proper-
ties of TFMSA. Neither dibasic acid wets PTFE, and the nominal
acid hydrates of both have lower vapor pressures than TFMSA·H$_2$O,
TFEDSA having the lowest vapor pressure of the three.
The conductivity data for the dibasic acids is not what might
have been expected intuitively. Unlike many dibasic acids,
TFEDSA is doubly dissociated even in fairly concentrated solu-
tions (ca. 0.25 N), as one can see from the conductance data
in Figure 1. However, in spite of the large apparant pK$_1$ and
pK$_2$, at equivalent normalities of 0.5 to 2 N, the dibasic
acids have somewhat lower conductivity than TFMSA, and in very
concentrated form these acids have only one-third the conduct-
ivity of TFMSA. From the fundamental point of view these
conductivities are surprising and from the technological
point of view, disastrous. This latter point is made of ap-
parant by the plot in Figure 2. This figure shows the con-
ductivity and concentration of acid in equilibrium with 200
torr water vapor, which is probably the highest water vapor
pressure practically sustainable in an operating fuel cell.

The conductivity of TFEDSA decreases on going from 90°C to 170°C, whereas the conductivity of H_3PO_4 in equilibrium with 200 torr water vapor increases on going from 100°C to 170°C. The net result is that at 170°C, TFEDSA has only one-fifth the conductivity of H_3PO_4 which would cause an unacceptable increase in cell stack IR losses.

Kinetic data for oxygen reduction on Pt in the new perfluoroethane sulfonic acids has been more difficult to obtain than physical property data due to the enormous influence of impurities. The most reliable data at present seem to be measurements with fuel cell type electrodes with supported Pt, which indicate the kinetics in 70 w/o TFEDSA are essentially the same as in 70 w/o TFMSA. Rotating disc data obtained in 0.1 N acids also indicates that the dibasic acid has the same weak adsorption property as TFMSA. However, there are unexpected effects of acid concentration on oxygen reduction kinetics in both TFMSA and TFEDSA. It has been known for some time that oxygen reduction kinetics on Pt decrease with H_3PO_4 acid concentration above ca. 1 M, but because of the specific adsorption of anion on Pt in this acid this concentration effect was presumed to be due to that phenomenon. But TFMSA and TFEDSA are not strongly adsorbing acids, yet concentration of these acids above ca. 0.1 N causes a dramatic decrease in activity (in spite of an increase in oxygen solubility with concentration!). Also the more detailed recent study of the anion effect in H_3PO_4 (3) showed that this effect saturates at ca. 1 M. There is clearly a recent accumulation of empirical observations that indicate our understanding of oxygen reduction kinetics in concentrated acid is not what many in the field have presumed it to be.

The technological implications of recent studies on TFMSA, TFEDSA, and DFMDSA are still unclear. While it is certain that none of these acids has the combination of physical and electrochemical properties to advance fuel cell technology, we do not yet know enough about the structure-property relationships in this family of compounds to predict the properties of even higher homologs than TFEDSA, i.e. the properties of longer chain multibasic perfluoroalkane sulfonic acids are still of technological interest. At the same time, new families of compounds should be considered as advanced electrolytes as well.

Acknowledgment

References

1. A. Adams, R. Foley and H. Barger, J. Electrochem. Soc., 124, 1228 (1977).
2. A. Appleby and B. Baker, J. Electrochem. Soc., 125, 404 (1978).
3. P. Ross and P. Andricacos, J. Electroanal. Chem., in press.
4. O. Petrie, S. Vasina and L. Lukyanycheva, Sov. Electro-chem., 17, 1144 (1982).
5. M. George, Technical Report, U.S. Army Mobility Equipment Research and Development Command Contract No. DAAK70-78-C -0103, December 1979.
6. W. Vogel, J. Lundquist, P. Ross and P. Stonehart, Electro-chim. Acta, 20, 79 (1975).
7. B. Baker, Final Technical Report, U.S. Army Mobility Equipment Research and Development Command, Contract No. DAAK02-73-C-0084, February 1975.
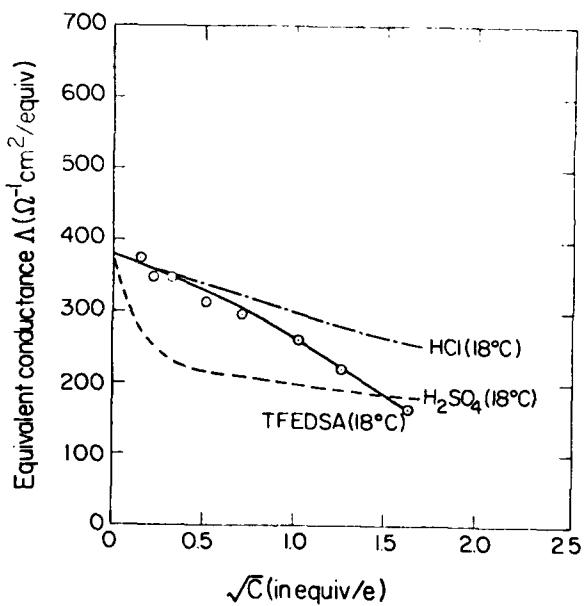
Figure 1. Conductance plot for TFEDSA compared to those for the strong, inorganic acids HCl and H_2SO_4.
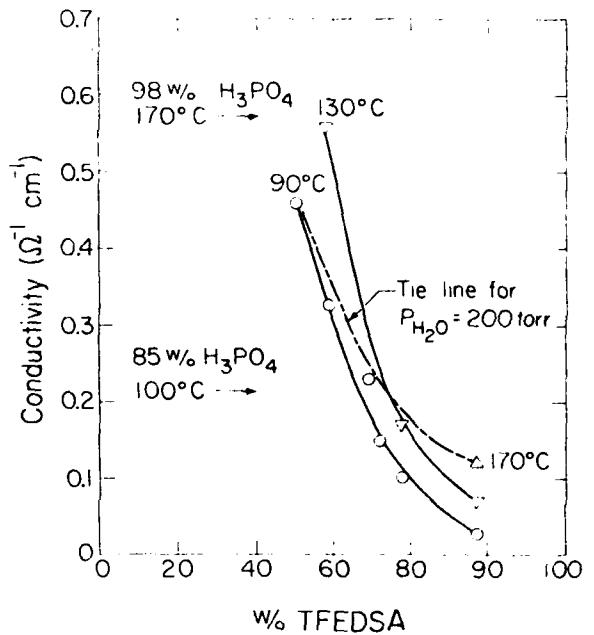
Figure 2. Conductivity of TFEDSA
solution as a function of
concentration and temperature.

AN OVERVIEW OF FUEL CELL DEVELOPMENT
UNDER THE MOONLIGHT PROJECT

Y.OGURA
Agency of Industrial Science and Technology
Ministry of International Trade and Industry
Chiyoda-ku, Tokyo,Japan

N.ITOH
New Energy Development Organization
Toshima-ku, Tokyo, Japan

Introduction

National research and development program on fuel cell
power generation technology,which belongs to the "Moonlight
Project", was initiated in August, 1981.
There are four types of fuel cell being developed by 1986;
phosophric acid fuel cell, molten carbonate fuel cell, solid
oxide fuel cell and alkaline fuel cell.
As the phosophoric acid fuel cellis expected to be commer-
cialized in early time to be initiated, 1000 kW class pilot
plants are to be built and tested in 1986.

Objective

The objectives of the Moonlight Project are to develop
highly efficient fuel cells which can use a variety of fuels
such as natural gas, methanol, coal-derived gas etc., and
may be applied to both small size dispersed generation to
large size centralized generation, so as to promote energy
conservation and reduction of oil dependency in electric
power generation field.
The commercialization of highly efficient fuel cell power
station would be a great impact on the power systems from
view points of energy conservation and extremely low contami-
nant levels.
To accomplish these objects, main effort is directed
toward the development of the phosophoric acid fuel cell
system,which has almost complated basic research stages on
component technologies in that time.
Also, molten carbonate fuel cell, solid oxide fuel cell
and alkaline fuel cell are to be developed respectively from
1981 to 1986.

Phosophric acid fuel cell

The phosophoric acid fuel cell may be possible to be commer-
cialized in early time to beintroduced.   Therefore, D&D and
demonstration on phosophoric acid fuel cell is given priority
over other types in the Moonlight Project.
On the phosophoric acid fuel cell, it is planned to deve-
lop full-scale fuel cells of high performance long duration,
and also to develop peripheral subsystems such as a fuel
processor which converts hydrocarbon fuel to hydrogen-rich

gas, reject heat recovery subsystem for cogeneration or
bottoming cycle application, and control & protection scheme
for fuel cell generation plant and interconnecting to power
systems.

Based on the results of the components development, 1000
kW class pilot plants will be designed and constructed in
1984-1985, and its test operation will be conducted in 1986.

Molten carbonate fuel cell

Because molten carbonate fuel cell may use coal-derived
gas as a fuel, it may contribute to reduction oil dependancy.

Molten carbonate fuel cell stacks of 5-10 kW scale are
planned to be developed and evaluated in 1986 whether a next
scaleup pilot plant could be developed.

A target of electrical power generation efficiency of
molten carbonate fuel cell system is over 45 %.

Solid oxide electrolyte fuel cell

Solid oxide electrolyte fuel cell may also use coal-
derived gas as a fuel, and contribute to a variety of fuels
utilization in electrical power generation field.

Basic research on it is planned to be done, and fuel cell
stack of 1 kW scale is scheduled to be demonstrated and
evaluated in 1986.

A target of electrical power generation efficiency of
solid oxide electrolyte fuel cell system is 50 %.

Alkaline fuel cell

Alkaline fuel cell may use only pure hydrogen gas as a
fuel. Alkaline fuel cell stack of 1 kW scale, which uses
air as oxidant and pure hydrogen as a fuel, is planned to be
developed in 1984.

A target of power generation efficiency of alkaline fuel
cell system is 45 %.

### Development target for phosophoric acid fuel cell

Two types of PAFC are under development by NEDO, one is
ordinary low pressure type for dispersed generation to be
under contract with MELCO and FUJI Electric Co. and the
other high pressure type for concentrated generation to be
under contract with Hitachi Ltd. and Toshiba Co..

The development targets for two types of PAFC are shown
in Table 1 and also the present status and future trend of
cell technology are shown in Figure 1.

	Dispersed Generation	Centralized Generation
Cell Operational Parameters		
Fuel	Natural Gas	Natural Gas
Operating Pressure	4 kg/cm^{2}G	6 - 8 kg/cm^{2}G
Operating Temperature	190°c	205°c
V-I Characterictics	0.7 V , 200 mA/cm^2	0.72 V , 220 mA/cm^2
Cooling Method	Water Cool	Water Cool
Fuel Processor		
Type	Catalytic Combustion	Pressurelized Conbustion
Efficiency	85 - 90 %	85 - 90 %
Performance Parameters		
Electrical Output Rating at AC terminal	1,000 kw	1,000 kw
Electrical Generation Efficiency (HHV base)	40 %	42 %
with Cogeneration	60 - 65 %	---
Operational Mode	Full automatic control (unmanned control)	one-man control
AC/DC Converter	Self Commutated	Self Commutated
Contaminant Levels	Nox $\lor$ 20 ppm $\lor$ 0.12 gr/kwh Sox $\lor$ 0.1 ppm	Nox $\lor$ 20 ppm $\lor$ 0.12 gr/kwh Sox $\lor$ 0.1 ppm
Noise Level	45 db at plant boundary	55 db at plant boundry
Power Response		
Cold Start to Standby	$\lor$ 4 hours	$\lor$ 4 hours
Normal Operating Range	25-100 % of rated power	25-100 % of rated power
Minimum to Maximum Power	$\lor$ 1 min	$\lor$ 1 min
Normal Plant Shutdown	1 hour	1 hour
Emergency Stop	$\lor$ 1 min	$\lor$ 1 min
Predicted dc Module Life	4 x 10^4 hours	4 x 10^4 hours

Table 1 Tactical Pilot Plant Parameters

Fig. 1. Present and Future Trend of Cell Technology
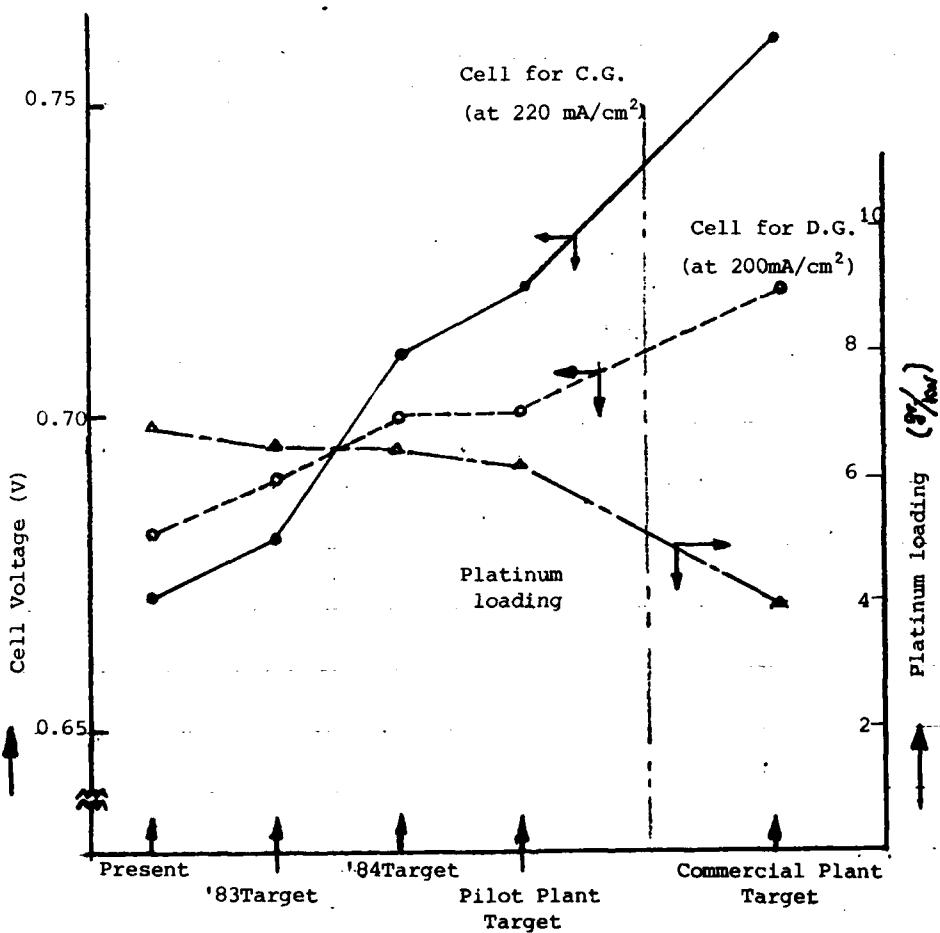
References:

1. L.Fukuda & N.Wakabayashi, "Status of Japanese Moonlight
    Project relative to Fuel Cell Research and Development"
    1982 Fuel Cell Seminar, Abstracts 15

R&D OF PHOSPHORIC ACID FUEL CELL TECHNOLOGIES
AND SYSTEMS FOR A DISPERSED POWER PLANT

K. KISHIDA   R. ANAHARA
Mitsubishi Electric Corp.   Fuji Electric Co.
Central Research Lab.   1-12-1 Yurakucho, Chiyodaku
8-1-1 Tsukaguchi-Honmachi   Tokyo, 100 Japan
Amagasaki, 661 Japan

1. INTRODUCTION

Mistubishi Electric Corporation, Fuji Electric Corporate Resesarch and Development Ltd. and Fuji Electric Co. were commissioned by NEDO to the Moon Light Project and have been performing research and development of phosphoric acid fuel cell technologies and systems for a dispersed power plant.

First, a conceptual design study of the system for a 1 MW plant was made. On the basis of the results, the targets of the specifications and the characteristics of the cell and the individual components of the plant were determined. Research is now being conducted of the technologies required to achieve these targets, being assigned as follows:
   *Cell technology----------Mitsubishi Electric Corp.
   *Stack Technology---------Fuji Electric Corporate
                                    Research and Development Ltd.
   *Fuel Reformer------------Fuji Electric Co.

In parallel with the component research and development, Mitsubishi and Fuji jointly conducted plant optimization studies and clarified the key specifications of a 1 MW plant. The detailed system design of the 1 MW plant is being carried out by Mitsubishi and Fuji on individual basis.

The major results sofar obtained through the project are discussed in the following chapters.

2. CELL TECHNOLOGY

A considerable effort has been made to improve cell performance. Material selection and process techniques of the major components of the cell, such as the catalyst, electrode, matrix and separator plate were studied. Research of the platinum catalyst, and its loading technique mainly to see the heat treatment effect on the carbon support as to the corrosion and sintering characteristics and stability, was performed to improve electrode performance and to increase cell life. Various kinds of materials for the matrix were examined and it indicated that the optimum average size of SiC particle and thickness of the matrix were 1 micron-meter and 100-130 micron-meters, respectively. Molding process of the separator plate was developed and the properties of the molded separator were found to be satisfactory.

An 11-cell-stack which had an effective area of 3,240 cm^2 was built and tested to demonstrate the improvement of the cell performance, mainly to verify the optimization of the manufacturing process condition for the individual elements. A compact cooler and some advanced sealing method were investigated and developed to ensure cell stacking. The test results of the 11-cell-stack and a typical small single cell are shown in Figure 1. The average cell output voltage of the 11-cell-stack is 0.661 volts at 200 mA/cm^2, meanwhile the single cell produces 0.73 volts under the same condition.
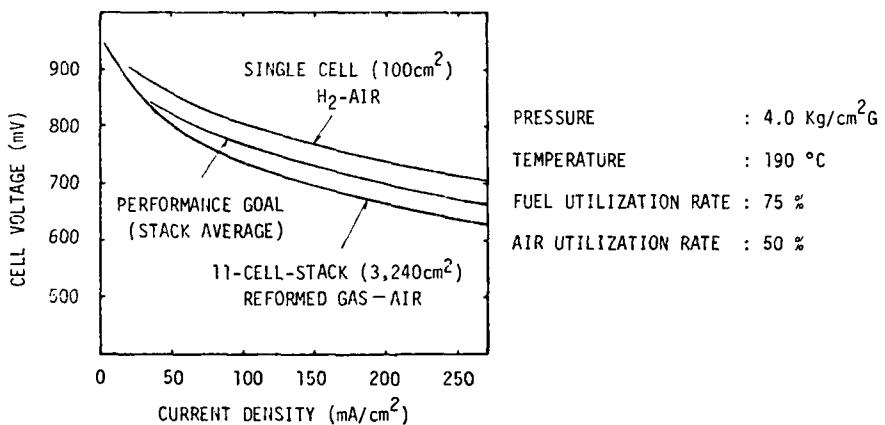
FIGURE 1. SINGLE CELL AND STACK PERFORMANCE

In parallel with the testing of several large-cell stacks, a number of small single cells are being exposed to endurance tests under various conditions including constant load test, cycle load test and thermal cycle test. No cognizable decay of the cell performance has sofar been observed for 6,000hr testing duration. (up to August 1983)

3. STACK TECHNOLOGY

The elemental technologies such as clamping, sealing and cooling technologies have been developed to realize reliable stacks easy to assemble. For these purposes the material characteristics of stack components such as ribbed substrates, separating plates, sealing materials and carbon plates for cooling purposes have been surveyed and the appropriate materials have been selected for the phosphoric acid fuel cell stacks. Based on such basic research works 2 models of 5-cell-stack having 1,000 cm^2 effective electrode and a 20-cell-stack of 3,600 cm^2 have been manufactured and tested. The performance of these models showed very similar characteristics to the small cell and

the difficulties in connection with the technologies of
clamping, sealing and cooling of bigger sized cell stacks
seem to have been fully solved.

4. STUDY OF FUEL REFORMER

A fuel reformer is required to be subjected to
combustion in a pressurized state, being necessary for
the construction of the system, and to allow stable
combustion under conditions in which the composition of
a burner fuel and the concentration of oxygen in a
combustion air will change according to load fluctuations
with reduced NOx exhaust. The purpose of this research
is to confirm these points experimentally.

A 1/10 scale model plant having equivalence to the
prototype specifications was already installed. Fuel gas
is prepared by mixing H_2, CO_2 and CH_4, at a fixed tempera-
ture (300-500°C), and supplied to a pressure combustion
burner. On the other hand, the pressure of the combustion
air is increased using an air compressor at a fixed temper-
ature (300-600°C), and the air is supplied to the pressure
combustion burner. To perform a pressure combustion test
three prospective burners will be selected from among
low-NOx burners, which are rated at about 50,000kcal/h.
Combustion gas from a pressure combustor is subjected to
heat exchange, and discharged into the atmosphere through
a pressure control valve, wich maintains the pressure for
the combustion process. The plant will begin the combus-
tion experiment from coming August 1983. Figure 2 shows
the pressurized combustor.

FIGURE 2. PRESSURIZED FURNACE
SECTION VIEW
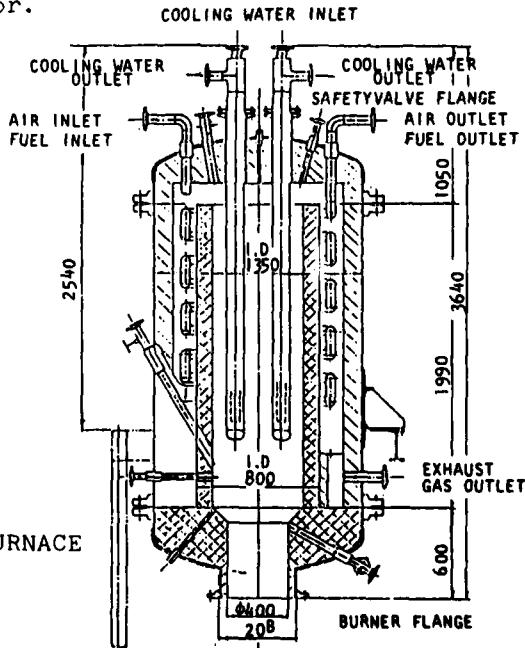
5. STUDY ON PLANT OPTIMIZATION

A preliminary system design of a 1MW plant which demonstrates the feasibility of a dispersed power generating plant installed in urban area has been studied. The principal objective of the design study is to pursue the highest efficiency of the plant under reasonable economical condition. Mitsubishi and Fuji have cooperated to fix the key specifications of the plant. Some of the results obtained so far are as follows.

1) To attain the system efficiency of 40%, an operating pressure of 3.5 $kg/cm^2 G$ or more is required, the maximum efficiency being reached at around the pressure of 4-5 $kg/cm^2 G$. (FIGURE 3)
2) The utilization rates of air and hydrogen are also optimized at the air utilization rate of about 60% and the hydrogen of about 80%.
3) At the steam carbon ratio (S/C ratio) of about 3-4 the maximum plant efficiency is realized.
4) To attain the system efficiency of 40% or more, the overall efficiency of a waste gas turbocompressor of 62% or more is required.
5) The partial load performance of the system can appreciably be improved by adopting the variable pressure operation.
6) In case the receiving pressure of the fuel (natural gas) is low the pressurized system equipped with a gas-booster yields higher efficiency than the low pressure system even in taking account the power consumption of the gas-booster.
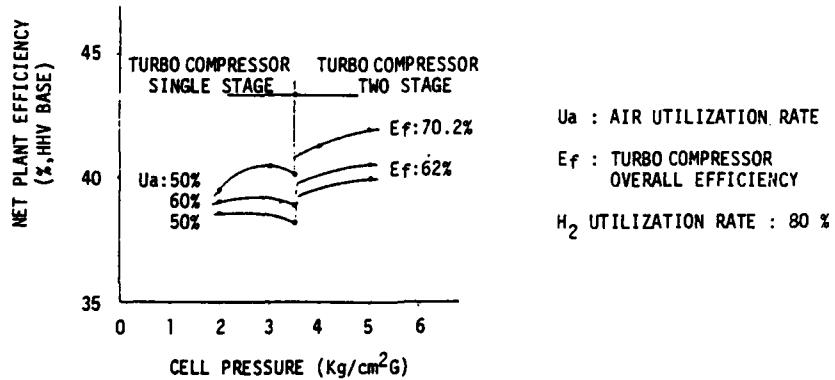

FIGURE 3. PLANT EFFICIENCY VS. CELL OPERATING PRESSURE

6. FUTURE PLAN

The Moon Light project plans to complete the final design of a 1 MW demonstration plant by Mitsubishi and Fuji by the end of FY.1983. The plant will be put into operation in 1986.

HIGH PRESSURE TYPE PAFC DEVELOPMENT
FOR CONCENTRATED GENERATION

S.Akimaru, Y.Tsutsumi, K.Tamura and S.Ono
Hitachi Ltd.
6 Kanda-Surugadai 4 chome, Chiyoda-ku,
Tokyo 101, Japan

K.Ogimoto, K.Sakamoto and N.Masunaga
Toshiba Corporation
13-12 Mita 3 chome Minato-ku
Tokyo 108, Japan

Since 1981, cell technologies and exhausted air combustion reformer system of high pressure type PAFC for concentrated generation have been developed by Hitachi Ltd, and Toshiba corporation respectively under the Moonlight Project.

I. Cell technologies*

Cell components were investigated. Very small size platinum particles were prepared by precipitation and then their growth was stopped in the colloidal state. Investigations are being conducted on a binary catalyst consisting of platinum and another metal element.

The ribbed substrates, as shown in Figure 1, were produced on paper making equipment. To increase tensile strength of the substrates, chopped carbon fibers were used. Manufacturing methods of substrates were examined to produce a product of uniform density and thickness.
Glassy carbon separators and mold carbon separators were tested. The former had smaller gas leakage properties than the latter.

A matrix was used to cover the catalyst coated substrate and separate the electrodes. Figure 2 shows microscopic photograph of the matrix made of metallic phosphate and silicon carbide. The metallic phosphate had a good affinity for phosphoric acid and good thermal stability. It has been successfully applied to large size cells.

During 1983, a high pressure type stack having more than 15 cells (0.36m^2 area) will be tested. Figure 3 shows the test facility under construction.

*Written by members of Hitachi Ltd.
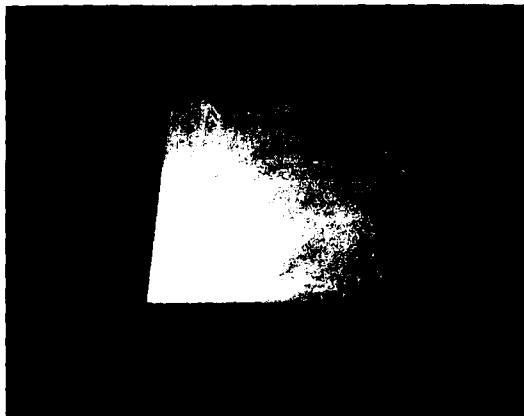
FIGURE 1 RIBBED SUBSTRATE   FIGURE 2 MATRIX MADE OF METALLIC
AND SEPARATOR   PHOSPHATE AND SIC

FIGURE 3 HIGH PRESSURE TEST FACILITY

II. Development of exhausted air combustion reformer system**

Toshiba corporation is developing 1MW PAFC power plant utilizing exhausted air combustion reformer system. As shown in Figure 4 comparing with conventinal system, low oxygen concentration exhausted air from fuel cells is used for combustion at a reformer burner in order to reduce air compressing power. System simulation shows this system will get more than 1% higher plant efficiency.

To realize the exhausted air combustion reformer system, it is firstly necessary to develope a reformer burner capable of combusting stably with low oxygen concentration air. In 1982 FY Toshiba fabricated a combustion testing device that is 1/4 scaled 50kW reformer burner to select adequate oxidation catalysts and to establish its packing method. Many kinds of catalysts were packed in single or double layer in this testing device, high temperature fuel gas and low oxygen concentration air simulating fuel cell exhausted fuel gas and air were supplied through these catalyst layers, and combusting process and its stability were investigated. The catalyst was packed in the form of two

EXHAUSTED AIR COMBUSTION   CONVENTIONAL REFORMER
REFORMER SYSTEM   SYSTEM
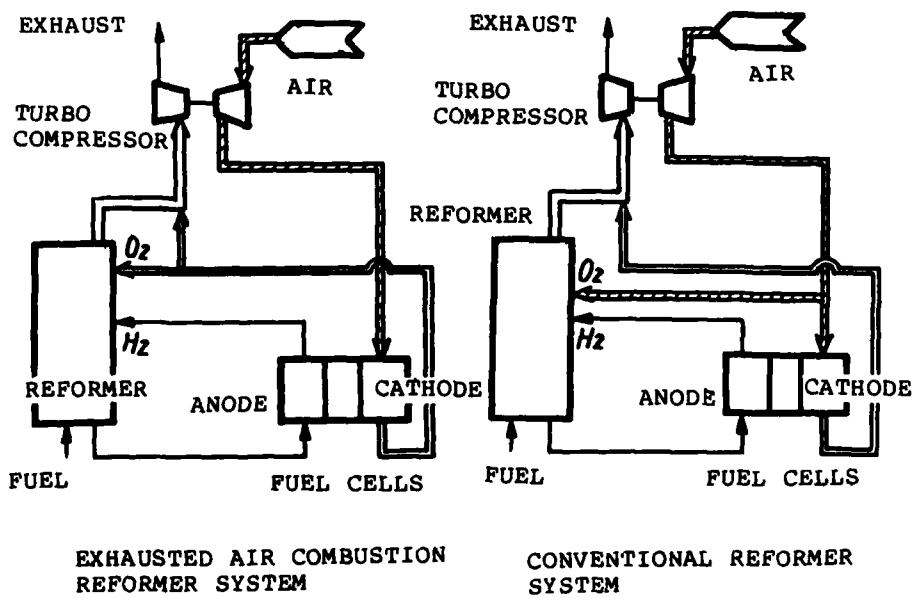
FIGURE 4 COMPARISON OF THE EXHAUSTED AIR COMBUSTION REFORMER
SYSTEM WITH CONVENTIONAL SYSTEM

**Written by members of Toshiba corp.

layers. Hydrogen is burnt in the upper layer. Under high
temparature obtained by hydrogen burning, methane is
completely burned in the lower layer catalyst. For example,
platinum catalyst is effectively used in the upper layer and
serium catalyst in the lower layer.

Based on the result of the above experiments 50kW
exhausted air combustion reformer was designed and
fabricated. Fig 5 shows this reformer.
In 1983 FY this reformer system is being evaluated.
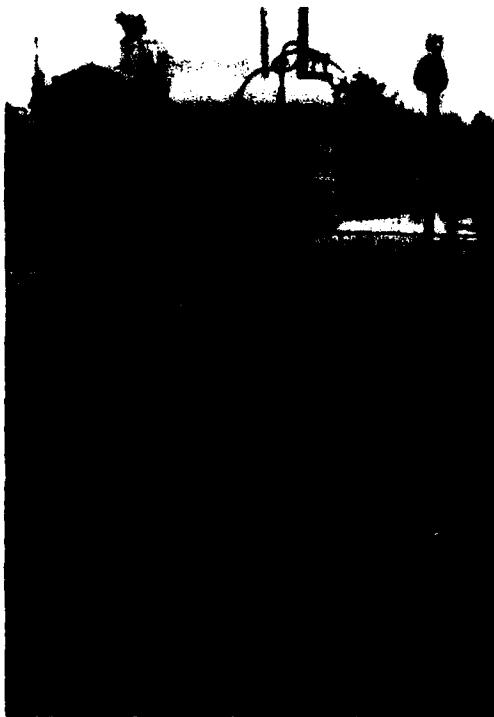
FIGURE 5 50KW EXHAUSTED AIR COMBUSTION REFORMER

DEVELOPMENT OF 50KW FUEL CELL POWER PLANT

T.Sakai, K.Tsukamoto, R.Saito, M.Ide
Sanyo Electric Co.,Ltd. Research Center
1-18-13 Hashiridani, Hirakata-shi
Osaka 573 JAPAN

Sanyo Electric Company has been developing fuel cells since 1959. Those developed include hydrogen-air fuel cells, methanol-air fuel cells and hydrazine-air fuel cells, some of them are used commercially. Since 1972, we have been developing phosphoric acid fuel cells (PAFC) for use in OS/IES (on site/integrated energy system) and electric utilities.In 1980 Sanyo made a cross licence agreement with ERC (Energy Research Corp. USA) to accelerate its development on the air-cooled PAFC system.

Recently we developed a 50KW natural gas fueled air cooled PAFC power plant whose specifications are given in Table 1, and whose design is shown in Figure 1. This power plant consists of a fuel processor, a fuel cell module and a controller.

A fuel processor which was developed jointly with TEC (Toyo Engineering Corporation) is of the steam reforming type, and is composed of a desulfurizer, a reformer, a shift converter and appropriate heat exchangers. The fuel is natural gas based city gas whose line pressure is reduced to 200mmAq at the fuel processor inlet. The conposition of processed gas is approximately H_2 : 80 % CO_2 : 19 %, CH_4 : 0.5 % and CO : 0.5 %.

A fuel cell module is composed of four stacks (a fuel cell stack is shown in Figure 2), and its DC output is 200 amperes at 250 volts. It is operated under atmospheric pressure at the temperature range from 180 °C to 190 °C. The fuel cell stack is air-cooled by utilizing cooling plates every 5 cells. Characteristics of the fuel cell are given in Figure 3.

The control system used for the power plant is a direct digital control system. Figure 4 shows the picture of the total power plant.

Based on the experience obtained through the operation of the 50KW power plant,a conceptual design for a larger scale power plant is being carried out to optimize both overall efficiency and plant economy.

Table 1.SPECIFICATION OF 50KW FUEL CELL POWER PLANT

Fuel Processor	Process	Steam Reforming
	Fuel	Town Gas (NG based pipe line gas) Inlet pressure:200 mmAq
	Catalyst	Reformer:Ni type LTS:Cu type
	Reforming Temp.	750 °C
	S/C	4-5
	Composition of Processed Gas	H_2:80%, CO_2:19%, CH_4:0.5%, CO:0.5%
Fuel Cell	Electrode Size	1,000 cm^2
	Catalyst	Platinum 0.7 mg/cm^2/cell
	Operating Temp.	180-190 °C
	Operating Pressure	Atmospheric
	Fuel Utilization	75 %
	Module Construction	4 Stacks
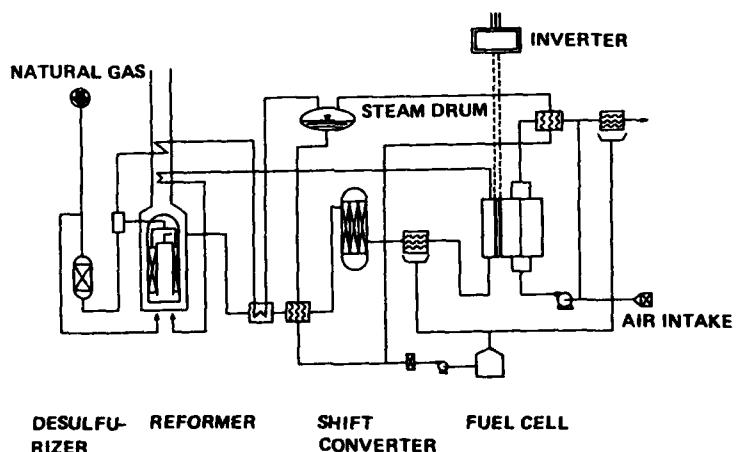
Fig 1. 50 KW FUEL CELL POWER SYSTEM SCHEMATIC
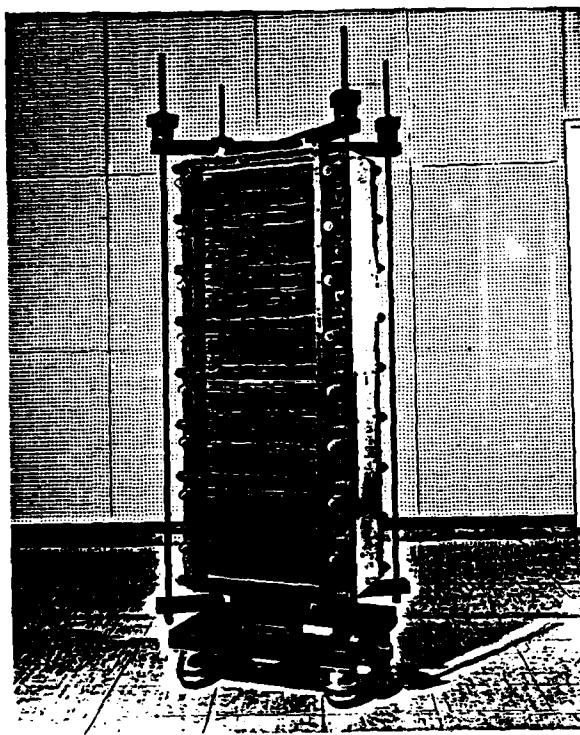
Fig 2.   FUEL CELL STACK
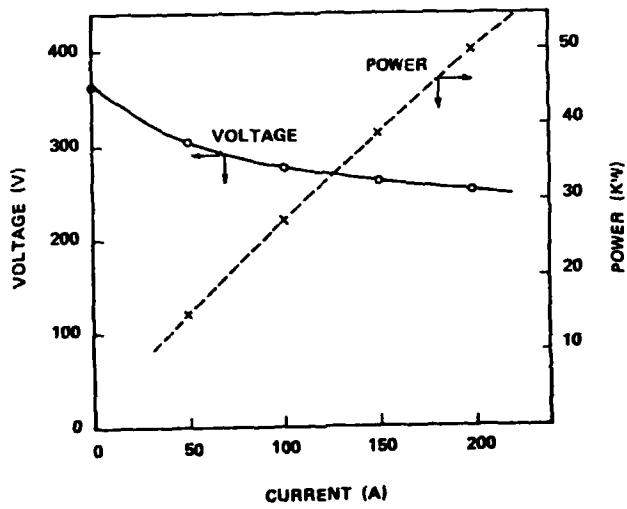

Fig 3.   CHARACTERISTICS OF FUEL CELL MODULE
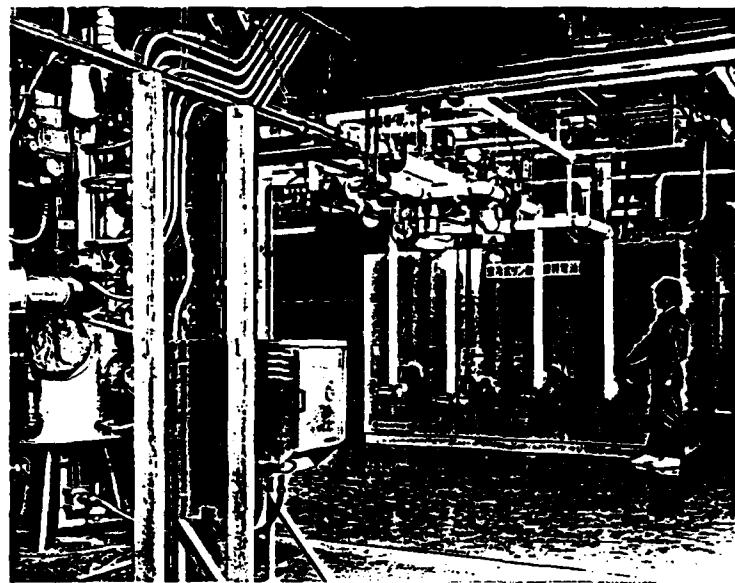
Fig 4. AIR-COOLED PAFC POWER PLANT

STATUS OF JAPANESE MOLTEN CARBONATE
FUEL CELL PROGRAM

T.Kodama
Government Industrial Research Institute, Osaka
1-8-31, Midorigaoka, Ikeda-shi 563 JAPAN

K.Tamura
Hitachi Research Laboratory, Hitachi, Ltd.
4026, Kuji-cho, Hitachi-shi 319-12 JAPAN

K.Murata
Toshiba Research & Development Center, Toshiba Corp.
4-1, Ukishima-cho, Kawasaki-ku, Kawasaki-shi 210 JAPAN

N.Horiuchi
Center Research Institute of Electric Power Industry
2-11-1, Iwato Kita, Komae-shi, Tokyo 201 JAPAN

INTRODUCTION

R & D program for molten carbonate fuel cell (MCFC) in Japan are being now promoted as a part of "Moonlight Project" by the Agency of Industrial Science and Technology, Ministry of International Trade and Industry.

Several kW MCFC stacks are planned to be developed in 1981-1986 (Phase I Project). An object of the cell performance is 150 mA/cm^2 at 0.8 V with 2000 cm^2 electrode. Next stage of the program (Phase II Project) will be R & D of 1000 kW scale demonstration plant to be judged depending on a result of evaluation of the stacks in 1986. A target of electrical power generation efficiency of MCFC system is over 45%. Implementing organizations are shown in Table 1.

Table 1. Implementing Organization

Organization	Main Activities
Government Industrial Research Institute, Osaka (GIRIO)	Surveying new material, Testing for evaluation
Central Research Institute of Electric Power Industry (CRIEPI)	System studies, Testing for evaluation
Toshiba R & D Center, Toshiba Corp. (TOSHIBA)	Cell and stack development
Hitachi Research Laboratory, Hitachi Ltd. (HITACHI)	the same as above

In addition, there are several cell and stack developers which are Fuji Electric Co., Ltd. (FUJI), Mitsubishi Electric Corp. (MITSUBISHI), Ishikawajima-Harima Heavy Industries Co.,

Ltd. (IHI), and Matsushita Electric Industrial Co., Ltd. (
MATSUSHITA).

In the following sections, some current topics of the R & D
program will be mentioned.

ELECTRODES

Development of high performance cathode is an important
target in Japan. Oxidized and lithiated nickel has been currently
used. The effects of various additives to nickel have been
tested at Hitachi.
Silver (5 atm %) and cobalt (5 atom %) additions have
shown higher current density-voltage performance and cell en-
durance than them of only nickel oxide cathode.

ELECTROLYTE SUPPORT MATERIALS

Fine alumina fiber (3μm in diameter) felt has been tested
for electrolyte support at Hitachi. The relation between the
making process of lithium aluminate from alumina and the allo-
trope of lithium aluminate have been examined. The result is
shown in Figure 1.
In addition to alumina fiber, potassium titanate fiber
(0.3μm in diameter) has been used.
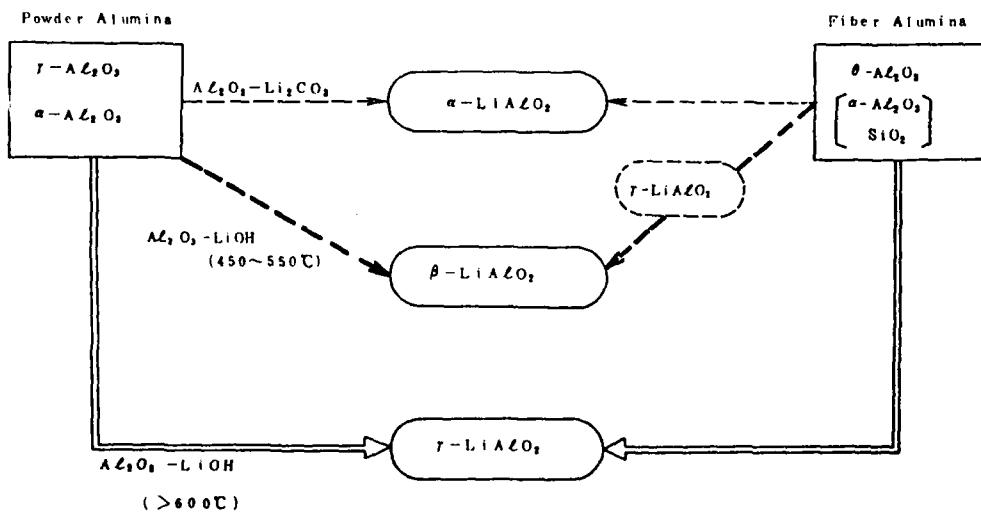
Fig. 1 Synthesis of Lithium Aluminate

EVALUATION METHOD FOR MECHANICAL STRENGTH OF HOT-PRESSED TILES

Non-destructive testing method was developed at TOSHIBA by means of ultrasonic pulse technique. Electrolyte tiles involved were hot pressed at 400-470°C, 300 kg/cm^2 without reinforcement, using mixed powders of 40 wt.% LiAlO$_2$ (14.4-17.8 m^2/g, γ-major) and 60 wt.% carbonate (Li$_2$CO$_3$/K$_2$CO$_3$ = 62/38 mol% eutectic). The tiles were typically 160 mm square and 80-97% theoretical density.

Figure 2 shows the relationship between a flexural strength σ (kg/mm^2, 3-points bending) and a density d (g/cm^3) of the tiles, which is expressed as $\sigma=8.94 \times 10^{-4}\exp(4.01d)$. Figure 3 shows the relationship between the longitudinal & transverse wave velocities at room temperature, v(L) & v(T) (km/sec) respectively, and density d, measured by ultrasonic pulse echo method, using 20 MHz quartz transducer (5mm in diameter). From these two velocity valus, shear modulus G, Poisson's ratio P and Young's modulus F can be caluclated by means of following equations:

$$G=dv(T), \quad P=1/2(v(L)^2-2v(T)^2)/(v(L)^2-v(T)^2), \quad E=2G(1+P)$$

Also, using v(L) vs d relation, density distribution of the tile, which is related to flexural strength, is measurable. This method was sufficiently applicable to non-destructive acceptance testing.
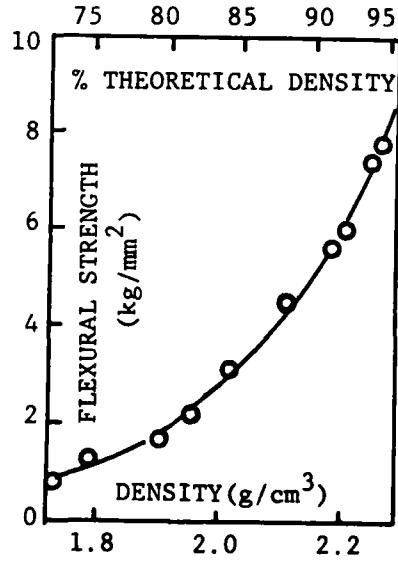

Figure 2. Flexural Strength vs Density
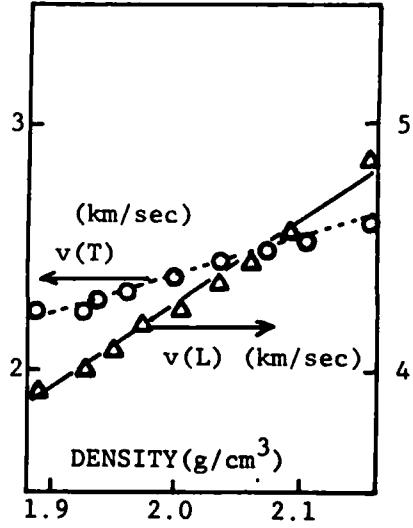
Figure 3. Wave Velocity vs Density

TEST FACILITY

CRIEPI has constructed a test facility for MCFC stacks and started experimental studies on July 1983. The facility is the first experimental one among the Japanese electric utilities. This is designed for the purpose of evaluating a technical development stage and studying future applications of MCFC power generation systems to utilities, industries, and so on. The basic specifications are as follows.

o Output of test cell : 1kW scale (up to 900 cm^2 electrode size)

o Electrical furnace : capacity 500$^\phi$ x 800^H 1 unit
                                        400$^\square$ x 300^H 1 unit

                     temperature up to 900 °C

                     pressure   up to 5000 mmAq

o Fuel gas : simulate gas

The facility will be used for interim evaluation of 1 kW scale MCFC scheduled on last FY 1984 in the Moonlight Project.
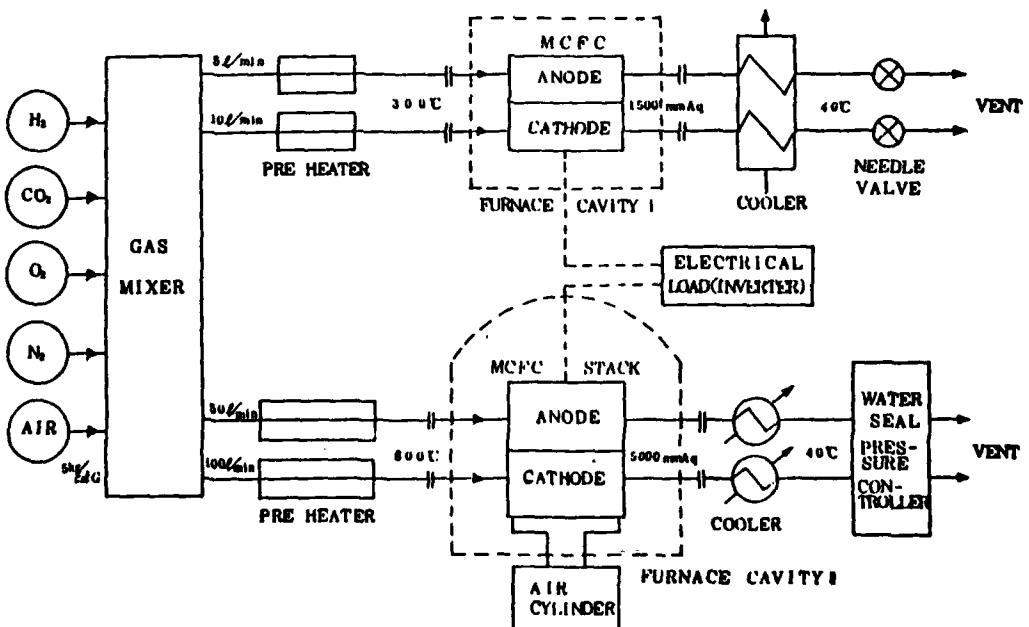

Figure 4. Test Fasility for MCFC

DEVELOPMENT OF HIGH TEMPERATURE SOLID ELECTROLYTE FUEL CELL AT ELECTROTECHNICAL LABORATORY

S.Nagata, Y.Ohno, Y.Kasuga, H.Sato
Electrotechnical Laboratory, Energy System Division
Sakura mura, Niihari-gun, Ibaraki, 305, Japan

Introduction

R & D program of the high temperature solid oxide electrolyte fuel cell with yttria stabilized zirconia (SOFC) in our laboratory had started 1974 as a program of hydrogen energy utilization under "Sunshine Project" (program to cope with energy shortage) promoted by Agency of Industrial Science and Technology of Japanese Government, but the fuel cell program including SOFC was transferred into "Moonlight Project" (program to develop energy conversion system with high efficiency) in 1981. The objective of the SOFC program is to investigate the basic characteristics of the cell through the fabrication and the power generation test.
The goal of the first stage of the SOFC program is to develop basic models of fuel cell stacks consisted of series-connected cells and to make a demonstration battery of 500-1000 W at the end of 1986 FY.

Cell Configuration, Materials and Fabrication

In the beginning, we tested the bell and spigot type cells, but the fabrication of the thin layers of the electrolyte was difficult, so we began to investigate thin layer type cells which were made on support tubes. As the method to make thin layers, the flame spray process was adopted. The output voltage and the power have been gradually increased with the improvement of the fabrication method and the appropriate selection of the electrode materials. The fundamental structure of the fuel cell stack is shown in Fig.1, the cells are fabricated on a alumina support tube, the outer diameter is 21 mm, the inner diameter 16 mm, the length 710 mm, the porosity 20 %, the thermal expansion coefficient 8.0×10^{-6}. In general, the calcia stabilized zirconia tube of which expansion coefficient is 11.5×10^{-6} is preferable on account of the matching to the expansion of other structural elements of the cell, but the calcia stabilized zirconia tube is weak against the thermal shock during the spray process, while the alumina tube is durable against the thermal shock, we adopt the alumina tube for these reasons. The effective length occupied by the fuel cells is about 320 mm in the middle of the tube. At first, alumina powder($-25+5~\mu$ m) is sprayed with the DC arc plasma spray process to assure gas tightness of the inter-connecting portions, the thickness of the layer is about 100 μ m. As the fuel electrodes, NiO powder (-170 mesh$+15~\mu$ m) is sprayed with the acetylene-oxygen thermo-spray process, NiO is to be be reduced into porous metal Ni with fuel gas, the thickness is

ALUMINA POROUS TUBE INTER-CONNECTOR

AIR ELECTRODE ALUMINA LAYER

ELECTROLYTE ALUMINA LAYER

FUEL ELECTRODE CURRENT LEAD

→ FUEL → OXIDATION PRODUCTS

→ OXIDIZER SOLDER

END CAP
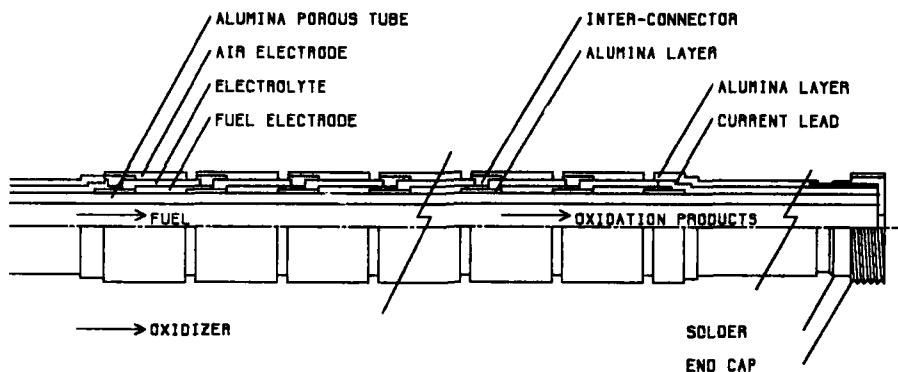
Fig.1 Cross-sectional view of a stack

about 100 μ m. As the electrolyte, yttria stabilized zirconia $(ZrO_2)_{0.92} \cdot (Y_2O_3)_{0.08}$ powder (10-50 μ m, mean 15μ m) is sprayed with the plasma spray process, the thickness is about 150 μ m. As the inter-connectors, Ni-Al powder (under layer) and $LaCrO_3$ (upper layer) are sprayed with the plasma spray process, but in the case of the short time test (100 hours), the upper layer is omitted, the layer thickness is about 100 μ m. As the air electrode, $LaCoO_3$ or the compound of lanthanum cobalt oxide doped with Sr or Ca is sprayed with the thermo-spray process, the thickness is about 150 μm. As the electrical current leads, Ni-Al powder is sprayed. And on these leads, alumina powder is sprayed to make the oxidation-resistive and gastight layers. At the both ends of the tube , the end caps are soldered to lead electric current to the metallic jackets which are cooled with water, and the jackets hold the cell stack and guide the fuel gas to the inside of the stack and exhaust the residual fuel and the oxidation-product. Fig.3 shows the finished fuel cell stack which is connected to the jacket.

Power Generation Test

The fuel cell stack was installed vertically in the test furnace with the jackets which were also fixed to the furnace lids electrically insulated from the furnace body. The furnace was heated at the rate of 50° C per hour to avoid the destruction of the stack due to the mismatch of the thermal expansion of structural parts of the stack. The oxygen was supplied from the top of the furnace, and the H_2 fuel gas was supplied through the top jacket, the water vapour and the residual fuel were exhausted through the bottom jacket. Fig.2 shows the output characteristics of the short time type stacks, the 20-cell stack, the 16-cell stack and the 12-cell stack, composed of $LaCoO_3$/YSZ/Ni. For the 20-cell stack and the 16-cell stack, the effective length was 320 mm , the active cell portions 5 mm and 8mm, and the

inter-connecting portions 11 mm and 12 mm respectively.
For the 12 cell stack, the effective length was 324 mm, the
active cell portion 11 mm, the inter-connecting portion 12
mm. The maximum output power of each stack was 47 W for the
20-cell stack , 57 W for the 16 cell stack and 49 W for the
12-cell stack. The highest maximum output power was obtained
in the case of the 16-cell stack. Concerning the output
power, the effect of the numbers of cells per effective
length of a stack agreed well with the numerical estimation.
Fig.4 shows the demonstration battery tested at the end of
1982 FY. The battery consisted of 11 stacks of 12-cell type,
and the stacks were connected electrically in series. Fig.5
shows the output characteristics, the upper curves (V1,P1)
show that obtained in the condition of oxygen and hydrogen,
and the lower curves (V2,P2) show that obtained in the
condition of air and hydrogen. The maximum output power of
260 W and 200 W were obtained in the each condition.
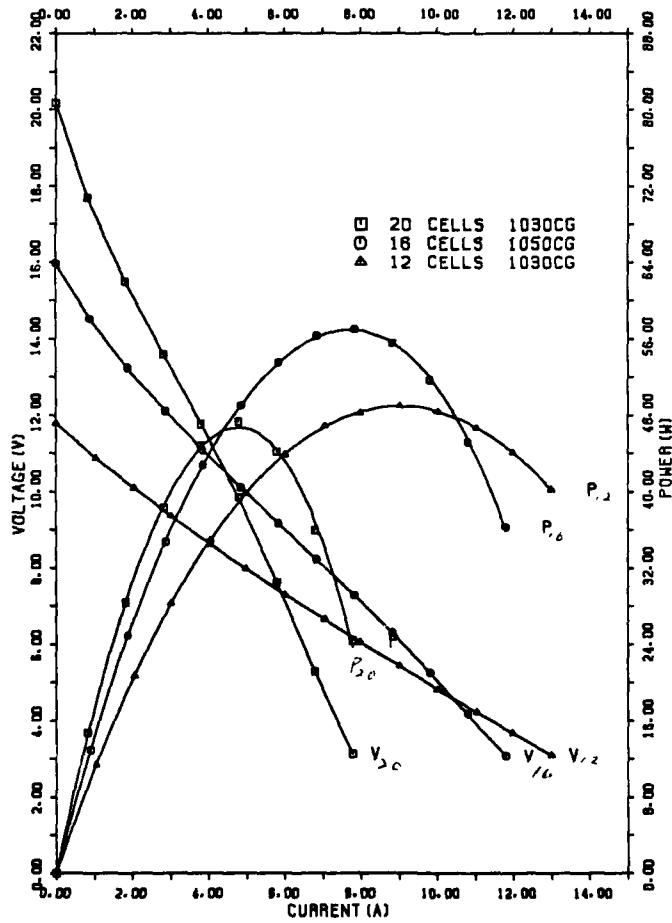
Fig.2 Output characteristics of three stacks.

167
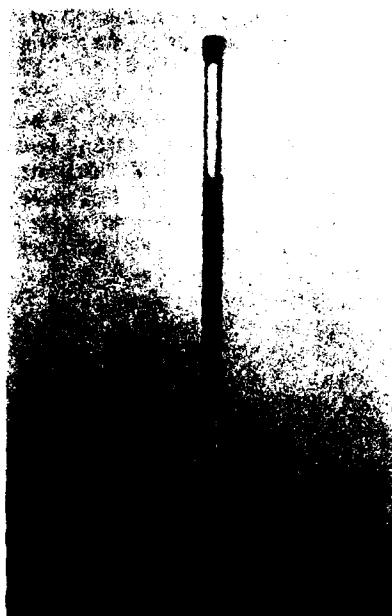
Fig.3 Finished stack.
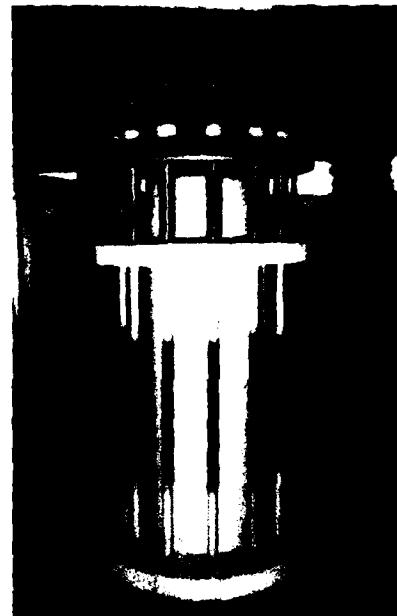
Fig.4 Demonstration battery.
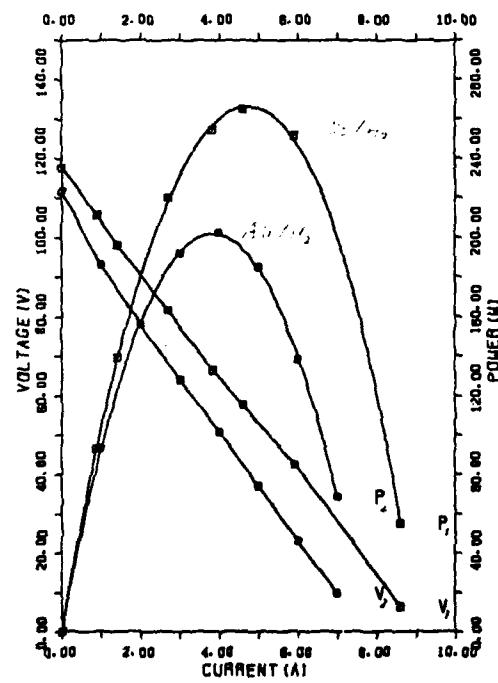
Fig.5 Output characteristics of the battery.

OPERATIONAL EXPERIENCES OF 30 KW
PHOSPHORIC ACID FUEL CELL POWER PLANT

M. Yonehara
The Kansai Electric Power Company Inc.
3-11-20 Nakoji, Amagasaki
Hyogo-ken 661, Japan

R. Anahara
Fuji Electric Company
1-12-1 Yurakucho, Chiyodaku, Tokyo 100, Japan

K. Suzuki
Fuji Electric Corporate Research and Development Ltd.
2-2-1 Nagasaka, Yokosuka, Kanagawa-ken 240-01, Japan

1. Introduction

In June 1980, The Kansai Electric Power Company Inc. and Fuji Electric
Co., Ltd. launched a joint project to verify the serviceability of fuel
cell power plant in the electric power system. The title of this joint
project is "The development of a small size phosphoric acid fuel cell
power plant", and a DC 30 kW (AC 27 kW) system was built by Fuji Electric
Co., Ltd. in October 1981. After the factory test of few months at
Kawasaki Factory of Fuji Electric, it was installed in the premises of
Sakai-ko Thermal Power Station of The Kansai Electric Power Company near
Osaka in April 1982.

After having the MITI's approval for a power generating facility in
December 1982, the plant began to distribute the electric power to an
auxiliary system of the station.

Since then the plant has recorded more than 3,000 hours of accumulated
operation by the middle of August of 1983, including 500 hours and 1,000
hours continuous (non-interrupting) operation by remote control.

The plant will operate under various conditions until coming December 1983
and will demonstrate the operability of the fuel cell power plant to the
utility grid system.

2. Plant specification

The key specifications of the plant are as follows.
     plant output: 27 kW (AC) 440 V, 60 Hz (30 kW DC)
     fuel   : air cooled, 190°C, 1 ata

minimum load :   25%
starting time: 4 hours from ambient temperature
all operation: fully automatic

The outerview of the plant is shown in Figure 1.

3.   Operation record

The plant has got the approval of Japanese MITI on December 1982, and
since then have been operating more than 3,000 hours (by the middle of
August 1983) with very satisfactory record.

Fig. 2 shows the relations between operating hours and the output of
plant, the voltage characteristics of fuel cell stacks, plant monitoring
system, starting up, shut down operation and also replenishment time of
phosphoric acid to stacks.

The description of each item is shown as follows:

(1)   Output of plant

0 - 190 hours (accumulated hours):   Total hours of
                         various test operations of short duration

180 - 2,000 hours: full load operation including
            100 hours, 500 hours and 1,000 hours continuous
            (non interrupting) operation by remote control

2,000 - 3,000 hours: continuous operation of 67% load

(2)   Stack performance

The v-i characteristic curve showed some decline tendency at the
initial stage of operation but after the replenishment of phosphoric
acid to stacks, which has been done on site after 1,000 hours
operation, the plant has been operating very stable and did not show
any decline of characteristics.

(3)   Plant monitoring system

As shown in Fig. 2 the plant was operated under 24 hour-monitoring
system by the Kansai Electric and Fuji Electric at the initial stage
but was shifted to remote monitoring under un-manned operation
gradually through the 8 hour-monitoring system (day time).

(4)   Starting up operation

Since the beginning of continuous operation the plant was started 11
times. The starting time from ambient temperature was about 4 hours
which was very close to design specifications.

The plant was loaded with the dummy resistance (dummy- load) and was connected to system under light load conditions automatically to protect the fuel cell from the deterioration due to high voltage on the cells.

(5) Shut down operation

Since the beginning of continuous operation the plant was shut down 10 times, 8 times of them were scheduled normal shut down. The plant was shut down two times under unscheduled conditions, one of which was the plant protecting shut down from the disturbance of line voltage and the shut down due to the trouble of the fuel cell plant itself was only once.
These emergency shut down is shown more in detail in next chapter.

(6) Contents of reformed gas

The contents of reformed gas did not show any big change through the operation.

(7) Contents of NOx

The NOx contents in the exhaust gas from the reformer was measured 0.06 gr/kwh under full load condition, which was very low compared with the design value of 0.24 gr/kwh.

4. Problems encountered and countermeasures

(1) Emergency shut down due to AC overcurrent

The plant was shut down due to the AC overcurrent on May 1983. It was found that the overcurrent was caused by the voltage drop of connected line due to the ground fault.

After this trouble the automatic voltage recorder was equipped to the line to have the detail data in case of similar line disturbances.

(2) Emergency shut down due to abnormal drop of water level in steam generator

The shut down happened on June 1983 by the abnormal drop of water level due to the water leakage from the standard joint of water pipings. It was understood the extra tightning was necessary. After the disassembling and inspection the plant was again assembled and the joint was further tightened after the high temperature operation.

(3) Carbon deposition in the preheater tubes

The deposited carbon was found on the inner surface of natural gas preheater tubes at the inspection after 300 hour plant operation.

Through decrease the temperature of preheater tubes the problem of carbon deposition was completely solved.

5. Future schedule

The plant will operate until coming December as follows.

(1) long term continuous operation at 67% load
(2) long term continuous operation at 100% load
(3) long term continuous operation at partial load

In each case the load change operation will be included experimentally.
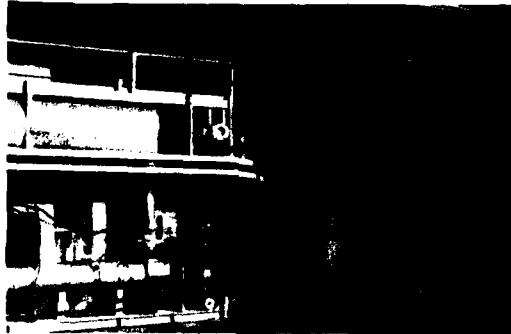

Figure 1   Outerview of 30 kW Plant
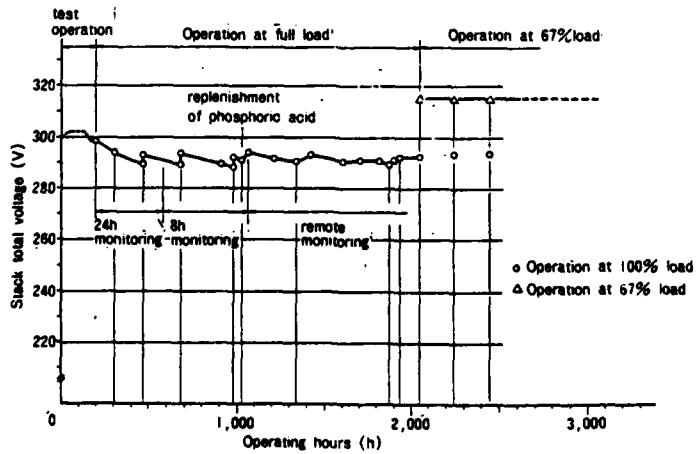
Figure 2   Performance of Plant Operation

APPLICATIONS OF FUEL CELL POWER
PLANTS IN JAPANESE UTILITY USE

N. Horiuchi
Central Research Institute of Electric Power Industry (CRIEPI)
11-1, Twato Kita 2-Chome Komae-shi, Tokyo 201, JAPAN

N. Itoh
New Energy Development Organization (NEDO)
Sunshine 60, 1-1, Higashi-Ikebukuro
3-Chome, Toshima-ku, Tokyo 170, JAPAN

and
S. Takeshita
Institute of Applied Energy (IAE)
Toshin Bldg. 1-13, Shinbashi,
1-Chome, Minato-ku, Tokyo 105, JAPAN

INTRODUCTION

The world economic recession and energy conservation would
put downward pressure on the increase rate of Japanese elec-
tricity demand. By the year 2000, however, peak demand and
electricity generated will grow to about 2.1 times and 2.4
times larger than those of 1982 respectively. In response to
the electricity demand increase, it is necessary to develop
electric power plants, which are cost effective, efficient,
reliable and environmentally acceptable, and inherent fuel
flexible.

The fuel cell power plant (FCPP) promises new power generation
technology which is expected to be commercially introduced
into the electric utility market in Japan by the late 1980s.
From the viewpoint of electric power supply and demand out-
look, this paper presents the estimation of the potential
market for FCPPs in Japanese utility use.

PROSPECT OF ELECTRIC POWER DEMAND

By the year 2000, electric power demand is estimated to be
1,120 TWh/y and 227 GW for peak demand, corresponding to
the growth of commercial, residential and public service use
with the elevation of living-standard.

PROSPECT OF ELECTRIC POWER SUPPLY

The utility industries are planning to import more LNG as
alternative fuel. By the year 2000, 31.5×10^6t/y LNG is ex-
pected to be newly available for LNG fired power plants of
23,000 MW capacity.

Both to secure electric power supply and to accommodate grow-
ing demand quickly, near site sitting new power generation
technology development is hoped to be successful in the near
future. Though multiple fuels can be selected for FCPPs,

natural gas is the most promising fuel for dispersed FCPPs, as regards fuel transportation system in Japan.

POTENTIAL DEMAND OF FCPPs REPLACING OLD OIL FIRED PLANTs

It is expected that old oil fired plants will be scrapped and LNG fueled FCPPs will be built. Oil fired power plants which were commissioned before 1959 are scheduled to be decommissioned by the year 2000. The capacity of such old oil fired plants which exist near the LNG storage tank yard, amounts to 2,750 MW. After 1995, these plants are likely to be replaced at the rate of 500 MW/y by FCPPs. The capacities of eight such plants are 156~600 MW.

POTENTIAL DEMAND OF DISPERSED FCPPs

Introduction of dispersed FCPPs for intermediate or peak load to the site of distribution substation (DS) contributes to reduce the cost of power transmission and distribution. Analysis of total daily load curve by substations (FIGURE 1) shows that 65% of total load is the load of DS (10~90 MVA). The DSs which have a low capacity factor, high ratio of peak to base load and constant peak demand account for 40% of the total DSs. Therefore dispersed FCPPs can replace as much as 26% of the total electric power demand.
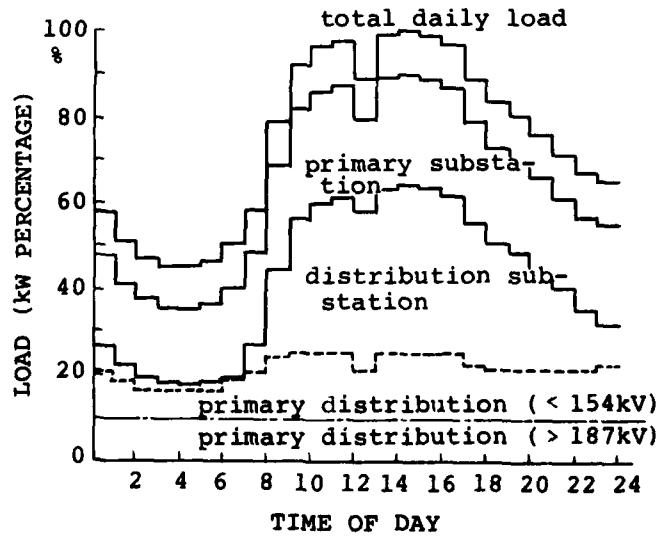

FIGURE 1. UTILITY LOAD PROFILE

POTENTIAL DEMAND OF ON-SITE FCPPs FOR INDUSTRIAL USE

The on-site fuel cell cogenerating plants (FCCPs) will be intro-
duced to the steel and nonferrous metals industries, ceramics
and stone quarrying (glass, cement, lime, etc.), rubber goods,
fiber, machine, food and paper pulp, those industries need
both steam and electricity (3).

In proportion to steam/electricity consumption ratio
(ton/MWh), three cases are considered.

     i)   purchase electricity and low pressure boiler for
        steam

    ii)   an independent conventional cogenerating
        plant

   iii)   FCCP and low pressure boiler for steam

Concerning these three cases, we drew a conclusion from the
appropriate premises which contain purchase cost of elec-
tricity, fuel price, low pressure boiler capital cost and
FCCP capital cost.

a)   There is no advantage or rationalization of fuel economy
    in the case of adding FCCP to the industry owned energy
    supplying existing system which has already got boiler
    plants.

b)   Both new installation of and replacement by FCCP, are
    profitable to the industry, if purchase cost of elec-
    tricity is higher than ¥20/kWh, fuel price is higher
    than ¥7.6/10^6cal and FCCP capital cost is lower than
    ¥170,000/kW (pay out time is 10 years).

c)   Introducing FCCP is less feasible for large scale in-
    dustries which have high steam/electricity consumption
    ratio.

d)   It is more feasible for small scale industries which have
    steam/electricity consumption ratio of 1∿5, consume expen-
    sive fuels (kerosene, fuel oil A, LPG), and have less
    than 300 employees.

The potential capacity demand is estimated at about 2,600 MW
by our analysis of statistical data (3),(availability factor
is 80%, 7,000 hrs/y).

POTENTIAL DEMAND OF ON-SITE FCCPs FOR COMMERCIAL OR RESIDENTIAL USE

Users that have both thermal and electric load or similar load pattern of heat and electricity are suitable for on-site FCCP, because of waste heat utilization. Potential users of FCCP are hotels, heated swimming pools, hospitals, restaurants, newly developed towns, and office buildings.

In Japan, there are about 40 businesses of district heating and cooling. On the other hand, most of the office buildings have made contracts with the electric power company for $2\sim3$ MW. Nevertheless, the large business buildings that need $10\sim20$ MW will increase by redeveloping the town or street. For the business districts where pipeline gas is available, thermal and electric energy consumption are almost equal and both load patterns are similar. So, FCPPs will be positively introduced into the office buildings.

In case of FCPP application, the economically transportable distance of steam/hot water, fuel cost and its supplying system should be examined thoroughly. Potential demand of on site FCCP for commercial and residential use is estimated at about 4,000 MW, in the case that the FCPP capital cost is ¥200,000/kW and fuel price is ¥$7/10^6$cal.

CONCLUSION

By $1990\sim1995$, phosphoric acid FCPPs are anticipated to occupy a few percent of the electric utility market.

By the year 2000, molton carbonate FCPP will be put to practical use. It is expected that FCPPs will occupy about 10% of the electric utility market.

In 21st century, we expect that $7\sim8\%$ of total electric power supply will be generated by FCPPs.

REFERENCES

(1) Electric utility industry council, intermediate report April, 1982.

(2) Conceptual design of fuel cell power plant for building utility use. CRIEPI Rept. 180039, June, 1981.

(3) Energy consumption composition statistics (MITI)